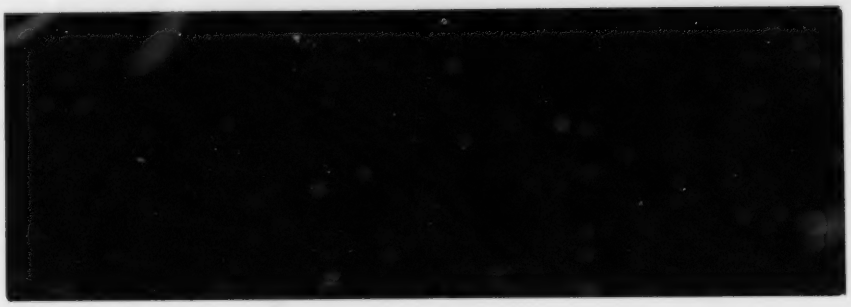

GULF CANADA RESOURCES LIMITED

FINAL REPORT

1988-1989

FUNDAMENTAL SUPPORT TO THE DEVELOPMENT OF GULF'S COAL BENEFICIATION PROCESS

By

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SUMMARY

The prime objective of this research contract is to investigate the effect of residuum properties on low rank coal upgrading by the Gulf Beneficiation Process. This research contract also evaluates two process options, on a preliminary basis, for enhancing product stability. The results of this research contract have established an important database in applying petroleum residua for the upgrading of low rank coals.

The effect of residuum properties on low rank coal upgrading was studied in details using five petroleum residua with a wide range of chemical and physical properties. The results show that the variations in both the chemical and physical properties do not produce any significant effect on product qualities and properties. Products prepared from these residua show very comparable product moistures and equilibrium moistures. Minor effects are noted with respect to reduction in pore volume, pore size distribution, and product stability as analyzed by the static oxygen sorption method.

The weight loss of residua was determined at 300°C in a TGA Simulator constructed specifically for this project. The results show that loss of residua at this temperature is minimal. This confirms that more effective utilization of residuum is achieved in the two-stage operation of the Gulf process wherein the residuum is added at temperatures of less than 300°C. Characterization of residua before and after the heating treatment, and extracted from products after coal beneficiation process also show that there are no significant changes in the physical properties. Irreversible bonding between the residuum and heat treated coals is not observed.

Two process options in an effort to enhance product stability were investigated on a preliminary basis. Experimental data obtained at different oxygen levels in the treating drum does not support the benefits of "Inert" atmosphere on product stability. Products produced by carbon dioxide post treatment suggest that this option should be further assessed. For complete stabilization of the product, this option may have to be incorporated with the reduction of moisture gap between the equilibrium and product moistures.

1.0 INTRODUCTION

This report describes work performed during 1988/89 on D.S.S. contract 06SQ.23440-7-9197, "Fundamental Support to the Development of Gulf's Coal Beneficiation Process."

Residuum is used in the Gulf Beneficiation Process to seal pores and coat surfaces of thermally dried coals. Initial development of the Gulf process (15SQ. 23440-3-9024) suggested that the level of beneficiation is dependent on the physical and chemical characteristics of the residuum. A proposal was submitted and this Research Contract was subsequently awarded to investigate this effect. The continuing development of the Gulf process into a two stage process, which applies residuum in a separate treating drum and at a lower temperature, has somewhat reduced the significance of residuum characteristics on coal beneficiation.

The Gulf Beneficiation Process is simple to operate and has the potential to be a very efficient upgrading process. Stabilization of the products however, remains the greatest challenge in process development. Stabilization of the upgraded products is the key in determining the technical feasibility of upgrading technologies for low rank coals. Recent experience gained from process development indicates that the drying medium and the post treatment of the upgraded products appear to offer more promise than residuum selection in enhancing product stability.

Considering the change in process scheme from single stage to two stage and the need to evaluate process options to stabilize upgraded products, several modifications of the program were proposed, discussed, and approved by the scientific authority assigned to this Research Contract. While the study of the effect of residuum properties remains to be a prime objective, the scope of the program has been enlarged to cover process options which may lead to a product of improved stability.

Specifically, treatment medium at high and low oxygen contents, and evaluation of product stability using an isothermal static oxygen absorption

method, were incorporated into this Research Contract. Obed and Highvale Coals were selected as the coal feedstocks to enable comparison of results obtained from this research contract with those from a previous study (06SQ.23440-6-9048).

This research contract consists of six tasks with the following specific objectives.

1. To analyse the coal samples selected for this Research Contract.
2. To characterize five residuum samples for physical and chemical properties.
3. To design, construct, commission, and operate a Macroscale Thermogravimetric Analyzer, "TGA Simulator."
4. To study the effect of heat treatment on residuum properties using the "TGA Simulator."
5. To determine the changes in residuum properties after coal beneficiation.
6. To study the effects of treatment medium, and residuum properties on the beneficiaiton of Obed and Highvale coals.
7. To characterize the upgraded products and relate the degree of beneficiation with residuum properties.
8. To evaluate the stability of the upgraded products.

The results of this research contract are discussed in detail in this Final Report. The work statement for this research contract is presented in Appendix 1.

2.0 EXPERIMENTAL

This section describes the equipment and procedures used in this research program.

2.1 Two Stage Coal Beneficiation Process

A two stage coal beneficiation process was used. The first stage involved heating the coal. The second stage involved applying the residuum. The overall process configuration is shown in Figure 1.

Heat Source and Control. The heat source was natural gas. The combustion gases passed through the heating drum and were then exhausted to the building's Roto-Cone air scrubbers. Fines entrained in these exhaust gases were not recoverable. A thermocouple inserted in the exhaust gases at the discharge end of the heating drum was used to control product temperature. Typically, the set temperature of the exhaust gases was 130 - 150°C above the desired coal temperature of 350°C. When the set temperature was reached the natural gas would shut off for either 7 or 45 seconds, depending on how quickly the exhaust gases cooled. The combustion air remained on at all times regardless of whether the natural gas was on or not.

Heating Drum. The heating drum was 1.6 meters in length and 20 centimeters in diameter. 2.5 centimeter lifters ran the full length of the drum with the exception of the initial 16 centimeters where helical flights served to slow down the incoming feed. Drum angle and rpm's could be varied to control residence time, which was approximately 10 minutes in a typical experiment.

Feed rate was controlled by an electromagnetic vibratory feeder. Product from the heating drum discharged through a chute into an insulated transfer auger which transported the hot product to the feed end of the treating drum. The amount of insulation and auger speed could be varied to control, within limits, the temperature of the coal entering the treating drum.

The temperature of the heating drum product was measured in the feed hopper of the transfer auger (T_1). The temperature of the treating drum feed was measured in the feed hopper of the treating drum (T_2). The difference between the two temperatures was typically in the range of 70 - 120°C.

Residuum Injection System. The residua were heated to about 300°C in a 5 litre container. Heat was supplied by a hot plate as well as by electrothermal heating tapes wrapped around the container. A Bran and Lubbe metering pump was used to deliver the hot residuum to the treating drum. The pump and a stainless steel tubing injection line (1 meter long and 0.95 cm diameter) were heat traced and insulated. The injection line projected about 10 centimeters inside the feed end of the treating drum. The hot residuum fell directly onto the tumbling bed of coal.

Treating Drum. The treating drum was 0.8 meters long, 20 centimeters in diameter, and had eight equally spaced 2.5 centimeter lifters running its length. Drum rotation was controlled by an electronic variable speed controller. Typical residence time was four minutes.

The treating drum product discharged into steel sample containers where final product temperature was determined (T_3).

Inert Gas System. In order to achieve a low oxygen atmosphere in the treating drum both nitrogen and carbon dioxide gas were injected through separate lances running the length of the treating drum. In a number of tests the supply of nitrogen was exhausted and it was necessary to inject CO_2 only during these tests. Holes drilled along the lances directed the gases at the tumbling coal. The gases were supplied from compressed gas cylinders.

Since the treating drum was open at both ends, maintaining a zero oxygen atmosphere was not possible. Initially, steam was injected into the treating drum but this made determination of oxygen levels difficult. Also, some condensation occurred which affected the flow of coal through the treating drum. Replacing the steam with nitrogen and carbon dioxide improved the situation. Injection of these gases resulted in an oxygen concentration gradient along the

drum. A Neotronics Portable Combustion Optimizer was used to establish the oxygen concentration profile (Figure 2) as well as to monitor the oxygen level during the low oxygen tests. The oxygen was monitored at the location corresponding to the lowest oxygen level established previously from the concentration gradient. It was assumed that the gradient/profile existed for all tests in which gases were injected.

Injection of the gases tended to cool the atmosphere inside the treating drum. The temperature inside the drum was determined at the mid-point of the treating drum immediately above the gas injection lances.

The operating procedure for this two stage pilot plant is as follows:

1. Fill the residuum supply container with the appropriate residuum.
2. Turn on the heating tapes and heat up the residuum, the pump, and the injection line.
3. Begin heating the heating drum.
4. Begin feeding coal when the residuum pump reaches about 120°C (outer surface temperature).
5. Adjust coal feed to desired rate, typically 500 - 600 g/min
6. When residuum reaches about 250°C turn on pump and adjust to desired rate, typically 16 - 20 grams per minute
7. When heating drum product temperature reaches 350°C and treating drum feed temperature reaches about 250°C, take a sample of treating drum feed for residuum calibration and immediately add residuum (see Section 6.1).
8. Insert residuum line into treating drum.
9. Monitor temperature and coal feed rate until treated product temperature exceeds 100°C.
10. Monitor residuum injection rate by visual inspection of residuum stream falling from the injection line onto the tumbling coal.
11. Wait a minimum of 15 minutes after treated product reaches at least 100°C.
12. Take timed sample of treated product, typically 10 minutes.
13. Take temperatures of treated product and treating drum atmosphere, while collecting treated product.

14. After collection of treated product take temperature of treating drum feed, then temperature of heating drum product.
15. If treated product rate and all temperatures are acceptable, terminate test or change conditions (see step 17).
16. If treated product rate or temperatures are not acceptable adjust conditions and repeat.
17. Allow conditions to re-establish (necessary due to interuptions in coal flow required for determination of coal temperatures).
18. Once conditions have re-established, begin injecting nitrogen and carbon dioxide.
19. Allow conditions to stabilize, approximately 10 minutes.
20. Begin collecting timed samples of treating drum product.
21. Determine temperatures as per step 13.
22. Monitor oxygen level in treating drum during sample collection.
23. After collection of sample determine temperatures as per step 14.
24. After collection of treated product samples allow the samples to air-cool to room temperature, approximately one hour.
25. Store cooled samples in nitrogen purged containers until required for analysis.

2.2 TGA Simulator

Residuum temperature at the point of application onto the coal particles during beneficiation is between 200°C - 300°C. Any light fractions of hydrocarbons initially associated with the virgin residuum may evaporate at the time of application. The portion of residuum left with the coal particles, therefore, may have different characteristics than the virgin residuum.

In order to determine the chemical and physical properties of heat treated residuum it was necessary to develop a system to generate sufficient quantity of residua for characterization. This system should also simulate the operation of conventional thermogravimetric analysis (TGA) for data comparison. A Macro-scale Thermogravimetric analysis (TGA) system which uses large quantities of residuum was developed in this research contract.

2.2.1 "TGA Simulator" System Components

The basic design of the "TGA Simulator" is a thermogravimetric unit capable of testing 50 gms of residuum samples. The design of the unit also allows the collection of gaseous and condensable hydrocarbons generated during heat treatment for analysis. Sufficient amounts of residua are available for characterization for physical and chemical properties after heat treatment.

Figure 3 shows the TGA Simulator designed and fabricated for this research contract. The major components of the TGA Simulator included the following:

- A Sartorius toploaded balance Model 1413 MP8 with accuracy of 0.01 gram and weighing capacity of 500 grams. The balance had built in system to compensate for temperature changes from 0°C to 100°C.

- A sample cup made of copper to hold about 50 grams of residuum.

- A free-standing glass platform to hold the sample cup inside the furnace and on the balance.

- A Thermolyne Tube Furnace Model 2125 with manual stepless heat input control, a pyrometer, and a temperature readout.

- A dynamic system to collect samples of (a) condensable and (b) gaseous hydrocarbons emitted by residuum during heat treatment.

- Oxygen and nitrogen flow controller to maintain levels of oxygen in the tube furnace (5 vol.% oxygen and 21 vol.% oxygen) during heat treatment.

- A precalibrated thermocouple, type K, and temperature readouts to display to 0.1°C changes in the temperature of the test sample.

2.2.2 Analysis of Samples and Products from "TGA Simulator"

Analysis of Residua After Heat Treatment

Residua after heat treatment in the "TGA Simulator" are characterized for softening point and penetration (Section 2.3). The results of these analyses are judged to be sufficient for measuring changes in the physical properties of residua due to heat treatment.

Analysis of Gaseous Hydrocarbons

An attempt was made to analyse the small amounts of gaseous hydrocarbons generated during the process of heat treatment. Gaseous hydrocarbons emitted at 300°C were collected by continuously drawing the gases from the sample cup, at a flow rate that did not affect the weight recording system.

Analysis of gaseous hydrocarbons was subcontrated to the Coal and Hydrocarbon Processing Department of Alberta Research Council. Gas chromatography with a thermal conductivity detector was employed to separate the C1 to C5 components.

Analysis of Condensable Hydrocarbons

A semi-quantitative analysis of condensable hydrocarbons collected from the TGA Simulator was also subcontracted to the Coal and Hydrocarbon Processing Department of Alberta Research Council. The technique of programmed gas chromatography (Varian Vista) with a capillary column (JW DB-1) and a flame ionization detector was used for the analysis. This analytical system has the capability to differentiate carbon numbers from C5 to C44. A chromatogram generated from standard compounds up to C44 was used as reference in this semi-quantitative analysis of condensable hydrocarbons.

2.3 Methods Used to Characterize Residuum Samples

Residuum samples selected in this research contract are characterized for physical and chemical properties. Most of the characterization was subcontracted to the Coal and Hydrocarbon Processing Department of the Alberta Research Council in Devon, Alberta. The methods used for the characterization and the subcontractors used are described below.

2.3.1 Physical Properties

- Viscosity was determined at two temperatures using a Brookfield Viscometer (ARC Coal Dept.).

- Density of residuum samples was determined by using a Pycnometer (ARC Coal Dept.).

- Softening Point was determined according to ASTM specification at CMRC.

- Penetration was determined according to ASTM specification at CMRC.

- Molecular Weight was determined using the Principle of Vapor Pressure Osmometry. A Carona Wescan Molecular Weight Apparatus was used. (ARC Coal Dept.).

- Thermogravimetric Analysis (TGA) data were determined at 21 vol.% oxygen and 5 vol.% oxygen content from ambient temperature to 350°C, at a programming rate of 20°C/min. A Dupont TGA Gravimetric Analyzer 951 and Data Acquisition Unit 1090 were used. (ARC Coal Dept.).

2.3.2 Chemical Properties

- Elemental Analysis was determined by using a Leco 600 Analyzer for carbon, hydrogen, and nitrogen. Sulfur content was analyzed by Leco SC32 Sulfur Analyzer (ARC Coal Dept.).

- Nickel and Vanadium were determined on the ash of the residuum samples. Ash was dissolved in sulfuric acid and determined by Inductive Coupled Argon Plasma Spectrometer (ICAP) at ARC Coal Dept.

- Crude Simulated Distillation was determined by dissolving the residuum in carbon disulfide (0.5 mg/ml) and compared with the profile generated from eight standard compounds in a gas chromatograph (ARC Coal Dept.).

- Component Types and Aromatic Ring Size were determined by Iatroscan Analysis (thin layer chromatography). This work was subcontracted to ARC, Oil Sands and Hydrocarbon Recovery Department. Residuum sample was dissolved in toulene (50 mg/ml) and elutriated with different solvents.

  n-hexane, methylene chloride and methylene chloride/methanol (98:2) were used for determining component types of saturates, aromatics, and polar compound. n-hexane, hexane/methylene chloride (90:10), and methylene chloride were used to distinguish aromatic ring size. Aromatics 1 are classified as compounds of three or fewer fused rings; and aromatics 2 are compounds with four or more fused rings. Polar A compounds are less polar than polar B which contains most of the asphaltenes.

2.4 Methods Used to Characterize Beneficiated Products

Numerous tests were done to determine various product characteristics.

2.4.1 Standard Analytical Tests

Several standard analytical tests were done to characterize the feeds and products. These tests included:

. Proximate Analysis	:	ASTM D 3172
. Ultimate Analysis	:	ASTM D 3176
. Calorific Value	:	ASTM D 2015
. Total Moisture	:	ASTM D 3302

2.4.2 Surface Area, Pore Volume, and Pore Size Distribution

Pore volume, and pore size distribution were determined by N_2 BET methods by Alberta Research Council, Coal and Hydrocarbon Processing Department. The determination was limited to pores of less than about 1000 $\mathring{A}$ in diameter.

Pore volume is measured directly from the volume of liquid nitrogen absorbed into the pores. Pore size distribution is calculated from the incremental volume absorption that occurs for incremental changes in pressure. It is assumed that a ΔP within a certain pressure range fills pores of only a specific size range. Pore surface area is calculated by assuming a cylindrical pore shape for all pores and calculating an area based on this shape and the average pore diameter determined (assumed) from the pore size distribution. Pore surface area is not discussed in this report because the data is simply a conversion of the pore volume data.

The pore structure determinations were run at room temperature. The procedure requires evacuation of the sample to eliminate moisture. When the treated samples were evacuated at elevated temperature an "oily" film appeared. This film affected the results such that pore volumes determined for samples evacuated at elevated temperature (as low as 100°C) were from 50% to 75% less than for samples evacuated at room temperature. It is believed that the combined conditions of vacuum and elevated temperature were sufficient to release some of the lower boiling point components of the residua, even though the simulated

distillation done on the residua indicated only very small quantities of such components (see Section 4.3). Evacuation of moisture at room temperature was consequently used for all the samples.

2.4.3 Equilibrium Moisture

The equilibrium moisture determination procedure was essentially the same as that specified in ASTM D 1412 with one difference: the true size consist was used instead of the minus 1.18 mm size fraction recommended by ASTM. This change was made because the residuum coating was supposed to seal the outer pores of the particles. Crushing the coated coal would expose fresh untreated surfaces. By using the full size consist the chances of error were increased due to sample heterogeneity. This potential problem was compensated for by increasing the weight of sample used per determination, 14-15 grams compared to ASTM's recommended 4-5. Test duration was 96 hours, which was longer than required for coals of Obed and Highvale rank. The longer time was used because it was felt that the residuum on the products would slow down the rate of moisture sorption.

2.4.4 Product Residuum Content

Representative product samples were pulverized to minus 60 mesh (0.25 mm). Approximately 3-4 grams of the pulverized sample was placed in a cellulose thimble and a standard Soxhlet Extraction with methylene chloride was used to determine the residuum content on the product. The amount of residuum was calculated by subtracting the final weight of dry extracted sample from the initial weight of moist, residuum coated sample, and then accounting for the moisture content of the sample.

A different procedure was used to extract the residuum from the 500 gram bulk samples (Section 5.3) because a reflux system capable of handling 500 grams of treated coal was not available. Consequently, each 500 gram sample was placed in a plastic jar which was subsequently filled with methylene chloride such that the entire sample was submerged. The jar was sealed and the sample soaked for at leat three hours. The sample was then poured onto a filter and the methylene chloride was retained in a second container. This procedure was

repeated five times for each 500 gram sample. The methylene chloride was then distilled from the residuum which was then heated at 100°C for 48 hours. The residuum remaining after this final heat treatment became the extracted residuum sample (Section 5.3).

2.4.5 Stability Tests

The stability tests were done by CANMET's Coal Research Laboratory Devon, Alberta. The tests were non-standard in that they were designed to handle full size consist coal. The tests measured a coal sample's ability to absorb oxygen and to generate carbon monoxide, CO, and carbon dioxide, CO_2. From the results it was inferred that the higher the oxygen sorption, expressed as ml's absorbed per 100g of sample, and the higher the CO and CO_2 production, expressed in ppm, the more reactive or less stable the coal. The test procedure was as follows:

- Remove 1.5 kg of sample from its sealed container.
- Place 1.5 kg sample in steel cannister of known volume (approximately 21.5 litres).
- Seal cannister and pass moist air through cannister for 5 minutes.
- Allow cannister and sealed sample to sit for 96 hours (isothermal).
- At end of 96 hours sample head gas in cannister and analyse using gas chromatograph.
- Calculate oxygen sorption and CO and CO_2 production values based on final and initial conditions.

3.0 COAL SAMPLE ACQUISTION AND ANALYSIS

Two coals were selected for testing:

- Obed Mountain High Volatile C Bituminous, Alberta Foothills
- Highvale Subbituminous B, Alberta Plains

The Obed sample was a dryer feed sample from the Obed coal preparation plant. Top size was reported to be 12.5 mm but some oversize was present. Accordingly, the Obed sample was screened through a 19 mm opening screen and the undersize was used. Table 1 presents the size distribution of the Obed coal used in the testwork.

The Highvale sample was taken from a raw coal stockpile at the Sundance power plant, Lake Wabamun, Alberta. The sample was screened, at site, through a 19 mm opening screen and the undersize was used for testing. Table 1 presents the size distribution of the Highvale sample.

The samples were stored in sealed nitrogen purged drums until required for testing.

The proximate, ultimate, and equilibrium moisture analyses of the Obed and Highvale coals are provided in Table 2. The difference between total moisture and equilibrium moisture is considered surface moisture. Thus, the Obed coal had 2.8% surface moisture and the Highvale coal had 0.4%. The surface moisture of the Obed sample was sufficient to cause flow problems when feeding the heating drum. Consequently, the coal feed rate fluctuated significantly during the tests using Obed sample.

The equilibrium moisture values reported in Table 2 are higher than values normally reported for Obed and Highvale coals, 11.5% and 18.5% respectively. Typically, coarser fractions exhibit lower equilibrium moisture values. Thus, equilibrium moisture values determined for full size consist Obed and Highvale coals are lower than the values determined for the minus 19 mm fractions used in this program.

Table 3 presents the pore volume and pore size distribution data for the Obed and Highvale coals.

4.0 BACKGROUND INFORMATION OF RESIDUUM SAMPLES

This section provides the physical and chemical properties of the five residuum samples used in this Research Contract. These data are obtained on the samples before coal beneficiation so that changes of properties due to heat treatment and after coal beneficiation can be compared. The five residuum samples selected and their sources are listed below:

Residuum	Source/Processing
Cenex PDA	Deasphalt unit from Cenex Corp. in Montana.
Koch 85/100	A soft asphalt used to make asphalt emulsion at Koch Industry in Toronto.
Suncor	Tar sand residuum obtained from Gulf's DRB Pilot Plant.
Peace River	Heavy oil residuum obtained from Gulf's DRB Pilot Plant.
CANMET Demo Pitch	Heavy Oil Residuum obtained from CANMET's Hydrocracking Process.

4.1 Chemical Analyses of Residuum Samples

The results of proximate analysis, elemental analysis, calorific value, and trace metal anlaysis for nickel and vanadium are presented in Table 4. The data were taken from D.S.S. Research Contract 06SQ.23440-6-9048, which was completed in March, 1988. It was felt that there was no need to re-analyse these samples in July, 1988 when the current Research Contract was initiated.

The proximate and elemental analyses show that while there are large variations in sulfur content in these residuum samples (2.0 wt% to 7.5 wt%), nitrogen contents remain fairly constant (0.6 to 1.3 wt%). The molar ratio of hydrogen to carbon indicates that CANMET Demo Pitch is the heaviest residuum used in this study (1.02). The CENEX and Koch asphalt are "lighter" residua showing a H/C ratio of 1.38 and 1.45 respectively. Despite the fact the Peace River and Suncor residua are from "Heavy" feedstocks, the H/C ratio of Peace River and Suncor are 1.41 and 1.45 respectively.

Nickel was determined in the range of 52 to 151 ppm, and vanadium content was determined in the range of 68 to 365 ppm. Koch asphalt has the lowest nickel and vanadium contents. CANMET Demo Pitch shows the highest concentrations of these two trace metals.

The calorific values of these residuum samples ranged from 9,290 to 10,160 cal/gm. Koch asphalt has the highest calorific value and CANMET Demo Pitch, being the heaviest residuum, has the lowest calorific value.

4.2 Physical Properties

The results of softening point, penetration, density, and viscosity of the five residuum samples are shown in Table 5.

Koch asphalt has the lowest softening point (47°C) and highest penetration (77). CANMET Demo Pitch, on the contrary exhibits the highest softening point (115°C) and lowest penetration (1). These data are supported by density determination and viscosity determination. It should be noted that temperature has a significant effect on viscosity. At 200°C, the large differences in viscosity observed at 150°C disappear. As the temperature in the treating drum is between 200°C - 300°C, the viscosity of all the residuum samples will be very comparable.

4.3 Molecular Weight and Simulated Distillation

The data of molecular weight and simulated distillation are presented in Table 6. Molecular weight determination provides an indication of molecular size and simulated distillation gives the initial boiling point and the amount of material remaining at 525°C.

While it was expected that CANMET Demo Pitch should have the highest molecular weight, in fact it gave the lowest molecular weight confirmed from repeated analysis. This may be due to the solvent (Pyridine) used in the determination. Pyridine is a highly polar solvent which may "dissociate" the "weaker" bonds presented in the CANMET Demo which has the highest nitrogen concentration. Apart from this deviation, the trend of molecular weight is in general agreement with the trend of the hydrogen to carbon molar ratio. The data of simulated distillation is discussed in Section 4.4 with the TGA data.

4.4 Thermogravimetric Analysis of Residuum Samples

Thermogravimetric analysis was performed at low oxygen content (5 vol.%) and high oxygen content (21 vol.%) on the five residuum samples. These data were generated to provide some background information on the effect of treating medium on residuum in the beneficiation experiments. The data are shown in Table 7 and the thermograms are provided in Appendix 2.

The results show that the change of environment from high oxygen to low oxygen content has little effect on the burning profile of these residua. Considering the fact that only milligrams of residuum samples were used, the oxygen content in the low oxygen atmosphere already exceeded the stoichiometric requirement. At 200°C weight loss was not detected. At 300°C appreciable amounts of residuum was lost while at 350°C, there was substantial loss of material. CANMET Demo Pitch gave the lowest weight loss in all the residuum samples studied.

Since the temperature of 300°C is an important temperature in this study and the oxygen environments give little effect on weight loss, the average

TGA weight loss at 300°C from low and high oxygen content are compared with the initial boiling point and weight loss at the end point (525°C) of simulated distillation in Figure 4 and Figure 5. Reasonable correlations are observed from the TGA analysis and the simulated distillation. The weight losses determined at 525°C by simulated distillation are also consistently higher than the weight losses determined at 300°C by the TGA technique.

4.5 Component Types and Aromatic Ring Sizes

The results of Iatroscan analyses of the five residuum samples are shown in Table 8. Iatroscan analysis is a semiquantitative classification of chemical components. This analytical method separates the residuum into saturates, aromatics and polar compound types. The data provides some insight of the nature of the components in a residuum sample and the average size of the molecules. The distributions of saturates, aromatics, and polars are shown in Figure 6.

The data indicates that Koch asphalt has the highest percentage of saturates, (20.8 wt%) which are the lightest compounds in the Iatroscan analysis. Cenex PDA has the second highest concentration of saturates (15.3 wt%). Residua from heavy oil and tar sands have much lower portions of saturates (8.2 wt% to 12.3 wt%).

The trend of aromatic components is not as clear as the saturates. They ranges from 32.3 wt% to 42.2 wt%. However, it should be noted that most of the aromatics in the CANMET Demo Pitch is aromatic Type 2, which consists of four or more fused rings. Aromatics 1 are mainly compounds with three or fewer ring structures.

Both the Koch asphalt and the Cenex PDA are low in polar compounds as expected (40.1 to 46.9 wt%). CANMET Demo Pitch contains 45.5 wt% of polars, whereas both Suncor and Peace River residua show a high concentration of polars. These are supported by the high heteroatom concentrations in the "heavier" residuum samples.

5.0 PROPERTIES OF RESIDUA DURING HEAT TREATMENT AND AFTER BENEFICIATION

The properties of the five residuum samples selected for this research contract are presented in Section 4, "Background Information of Residuum Samples." One of the prime objectives of this research contract is to investigate the effect of change of residuum properties during coal beneficiation. TGA Simulator experiments were carried out to examine the effect of heat treatment on residuum, and residua were extracted from beneficiated products to determine their final characteristics. The commissioning of the TGA Simulator, the results from the TGA Simulator experiments and the properties of residua after coal beneficiation are described in the following sections.

5.1 Commissioning the TGA Simulator

The conventional thermogravimetric analysis (TGA) used a heating rate of 20°C/min, and the residua were heated to a maximum temperature of 350°C under two levels of oxygen concentrations (5 and 21 volume % of oxygen). A number of experiments were carried out to investigate if the TGA Simulator could be operated in the same manner.

5.1.1. Calibration of Furnace

The furnace used in the TGA Simulator system was tested at different control levels to establish the heating rate of the furnace. The furnace temperature as a function of time was monitored at three different settings and the results are shown in Figure 7. Figure 7 shows that heating rates of 13°C/min, 31°C/min, and 50°C/min were obtained. The setting which gave 31°C/min heating rate was used in the commissioning experiments, as this heating rate was expected to give a heating rate of 20°C/min for the residuum.

5.1.2 Preliminary Commissioning Experiments

The preliminary commissioning experiments were carried out using the Cenex PDA. A thermocouple was inserted into the residua, and a furnace heating rate of 31°C/min was used in the experiments.

Three problems were encountered in these preliminary commissioning experiments. Firstly, it was found that thermal equilibrium between furnace and residuum temperatures was not established, and that the residuum was heating at a lower rate than 20°C/min. Secondly, when a constant furnace heating rate was maintained the temperature of residuum exceeded 300°C. Thirdly, a hard crust was formed on the surface of the residuum and the thermocouple was held by the crust, resulting in interference when recording weight loss as a function of time. The problems encountered during these tests suggested that new methods for carrying out the TGA Simulator tests needed to be developed.

5.1.3 Development of Testing Methods for TGA Simulator

It became quite apparent that it would be difficult to carry out the TGA Simulator under the same conditions as the conventional TGA. Since the maximum temperature (300°C) was more important in heat treatment than the rate of heating, it was decided that a procedure should be developed for achieving the maximum temperature of 300°C for the residua.

Since placing a thermocouple in the residua interfered with the recording of weight loss, which is important data measured from the TGA Simulator, the thermocouple inserted in the residua had to be removed. The elimination of the thermocouple inserted into the residua was possible only if the temperatures of the residua could be accurately predicted from the temperatures of the furnace.

The relationship between furnace and residua temperature was checked for a number of experiments targeted for a maximum temperature of 300°C for the residuum. This maximum temperature was achieved by first slowly heating the sample to a residuum temperature of 130°C. The heating rate was increased to 31°C/min for the furnace until the temperature of residuum reached 260°C. Heat input was reduced at this point until the temperature of the residuum stabilized at 300°C.

The relationship between the furnace and the residuum temperature using this operating method under high and low oxygen environments is shown in Figure 8.

5.2 TGA Simulator Experiments

The TGA Simulator was operated to monitor loss of weight of residua, provide insight to the hydrocarbons generated during heat treatment, and produce heat-treated residua for characterization of physical properties. The data obtained from the TGA Simulator is also compared with the conventional TGA.

5.2.1 Weight Loss from TGA Simulator

Weight loss of the five residua were determined from 260°C to 300°, using the procedure developed in Section 5.1.3. It was found that only small weight losses were detected. Weight loss determined under high oxygen content (21% volume) were consistently higher than those determined under low oxygen condition (5% volume) for all the residua studied in this program.

Under high oxygen atmosphere, the lightest residuum, Koch 85/100, gave the highest weight loss (2.3%). This is followed by Cenex PDA (1.0%), the second lightest sample. Residua from Suncor and Peace River gave weight losses of 0.64% and 0.38%, respectively. The heaviest residuum, the CANMET Demo Pitch, only showed a weight loss of 0.14%.

The same trend of weight loss was observed under low oxygen condition. The data is presented in Tables 9 to 13, inclusive.

5.2.2 Conventional TGA vs. TGA Simulator

The results of conventional TGA and TGA Simulator at 300°C under two oxygen levels are compared in Table 14 and Figure 9.

While both the conventional TGA and the TGA Simulator were operated at the same final temperature (300°C) the actual environments of these experiments were actually quite different. The TGA Simulator used large quantities of samples which tended to restrict the burn off of residua at the surface. A hard crust was observed at the surface; and the differences between

weight loss under high oxygen environment and low oxygen environment were also greater. The weight losses determined under high oxygen content were consistently greater than those determined under low oxygen content.

The conventional TGA, on the other hand, only used milligrams of samples. The oxygen contents under both high and low oxygen contents were greater than the oxygen contents required stoichiometrically. The complete exposure of the residua to oxygen, therefore, gave similar results under both oxygen atmospheres.

Comparison of the data from conventional TGA and TGA Simulator shows that there is a good correlation for Koch 85/100 asphalt, but as the residuum becomes heavier, the correlation deteriorates.

5.2.3 Hydrocarbons from TGA Simulator

Both gaseous and condensable hydrocarbons were collected in the TGA Simulator experiments. While an attempt was made to identify the components in the gas samples using the technique of gas chromatography, the small amounts of gases collected from the residua made the analysis virtually impossible. Therefore, no analyses were available.

The analysis of the condensable hydrocarbons reveals that compounds of various molecular weight were generated under heat treatment of residua at 300°C. The chromatograms obtained at high and low oxygen contents are also substantially different (Appendix 3). These chromatograms appear to support the "film" reaction at the surface of the residua with oxygen in the TGA simulator experiments.

These chromatograms provide semi-quantitative determinations of the components in the condensable hydrocarbons. While on a weight basis the condensable hydrocarbons are relatively unimportant, the data obtained from this analysis provides some useful insight on the change of residuum properties. The changes of chromatographic patterns obtained for the individual residuum samples are quite different.

The condensables collected for Koch 85/100 asphalt under high and low oxygen contents are essentially identical. They consist of the hydrocarbons essentially from C10 to C36, with compounds between C5 to C10 detected under high oxygen content.

The chromatograms obtained for the Cenex PDA under high and low oxygen contents are drastically different. C11 to C36 are almost uniformly distributed under low oxygen content; but much higher concentrations of compounds between C14 to C32 were detected under high oxygen content condition with only minor concentrations of higher or lower carbon compounds.

Residua from heavy oil operations also show significant changes in the chromatograms under high and low oxygen contents. CANMET Demo Pitch shows a chromatogram mainly with C24 plus material under low oxygen content and condensable materials mainly between C11 to C24 under high oxygen environment. Both the Peace River and Suncor residua show similar results by converting higher carbon content compounds into components mainly in the C18 minus fractions as the oxygen environment increases.

5.2.4 Physical Properties of Heat Treated Residua

The residua after the TGA simulator experiments were recovered and examined for softening point and penetration. The data are presented in Table 15, which compares the data obtained on virgin residua, residua after heat treatment, and residua extracted from products after beneficiation (see Secton 5.3).

These data show that there are virtually no changes in both softening point and penetration. These data support the observations that reactions between oxygen and residua only happen at the surface in the TGA simulator experiments.

5.3 Residuum Properties After Coal Beneficiation

The residua deposited on the coal surface and penetrated into coal pores during the beneficiation process were extracted for examination of physical properties. A 500 gm sample was used to provide sufficient quantity of residua for characterization of physical properties.

Residuum contents determined by this "large scale" extraction using methylene chloride are compared with the results obtained from soxhlet extraction. A reasonable comparison was obtained and is shown in Table 16.

The data of the softening point and penetration of the residua extracted from the product are compared with the virgin materials and with the residua recovered from the TGA simulator in Table 16. Typically, the softening points were highest for the residua extracted from the coal for all residua except the CANMET Demo Pitch whose softening point decreased. The penetration values were not as consistent but tended to be lower than the virgin materials as well as the TGA Simulator samples. The Koch 85/100 asphalt showed a significant reduction in penetration, (36-44 compared to 77 for the virgin asphalt).

6.0 BENEFICIATION EXPERIMENTS

The procedure used for the beneficiation experiments is provided in section 2.1. The following observations relate to the actual performance of the beneficiation tests.

Several factors influenced the operation of the Beneficiation Pilot Plant. Among these are the control of exact resdiuum application rate, control of product temperatures, and the maintenance of low oxygen atmosphere in the treating drum. The effects of these factors and the operating data for the Final Beneficiation Experiments selected from numerous experiments are discussed below.

6.1 Residuum Application Rate

Product residuum content was affected by the raw coal feed rates which fluctuated at $\pm$ 50 gm/min. The coal feed rate to the treating drum was affected by the amount of fine particles entrained in the drying gases, and by the extent of partial combustion and devolatilization of the low rank coals in the heating drum.

The major difficulties in delivering an exact amount of residuum in the experiments were the plugging of residuum feed line and the lack of a proper pumping system at the desired capacity.

Initially, the metering pump was fitted with a 5 mm plunger and had a maximum output of about 50 grams of residuum per minute. The small check valves used in conjunction with the 5 mm plunger were not suitable for the hot residuum. Consequently control of residuum rate was very difficult and complete stoppage occurred frequently during a test. The 5 mm plunger was replaced with a 42 mm plunger and a more appropriate valve system with respect to the hot residuum application. However, the larger plunger had a maximum output of about 3.5 kg per minute. This capacity was much higher than was required in the Beneficiation Experiments.

Operating under such conditions, typical fluctuations in pump feed rate were ±2 grams per minute, or about 10 to 12% of desired flow. This system was used in the Experimental Program because although precise control was not possible with the larger plunger, the problem of complete stoppage was significantly reduced, although not completely eliminated.

6.2 Control of Product Temperatures

The temperature of coal leaving the heating drum (T_1, Figure 1) was typically about 350°C. The temperature of coal entering the treating drum (T_2) was about 250°C. Since there was no other heat source in the treating drum, the product temperature (T_3) fluctuated between 70°C to 160°C, depending on the duration of the experiments, the injection of inert gases which created a cooling effect in the treating drum, and the temperature of the feed entering the treating drum.

In order to standardize the Beneficiation Experiments, treated product samples were not taken until the treated product temperature reached 100°C, which took about two hours from the time the coal feed was started. If conditions were acceptable then the test was completed. If conditions were not acceptable the test was continued, at times for several hours, until the conditions were acceptable. For these prolonged tests the treating drum was continuously heating up due to the incoming hot feed coal. Consequently, the longer it took to complete a test, the hotter the product temperature became due to the heat build-up in the treating drum.

6.3 Low Oxygen Atmosphere in the Treating Drum

Nitrogen and carbon dioxide were injected along the length of the treating drum in order to reduce the oxygen content in the drum. In a number of tests carbon dioxide only was injected. Oxygen levels were determined at the same location for each test. A typical oxygen profile inside the drum is shown in Figure 2. Since the tests were run with continuous feed to and product withdrawal from the treating drum, it was not possible to completely eliminate oxygen from the treating drum. In addition, the fact that the drum rotated made sealing against

oxygen infiltration impossible. The volume of gas that could be injected was, to a certain extent, limited by its undesireable cooling effect.

6.4 Operating Data of Selected Beneficiation Experiments

With the limitations experienced in resdiuum application, product temperature control, and the maintenance of low oxygen environment, twenty experiments were selected from numerous runs based on the level of residuum content, acceptable product temperatures, and the acceptable oxygen level in the treating drum. The operating data for these selected experiments is shown in Table 17.

Residuum contents determined on the products in these selected experiments range from 2.6 wt. % to 5.4 wt. %. Product rates vary from 225 to 368 gm/min. The minimum oxygen levels achieved in these experiments range from 0.4 to 4.2 vol. %. The coal temperatures at various stages of treatment are also tabulated in Table 17.

The qualities and properties of the samples obtained from these selected experiments are discussed in Section 7.

7.0 PRODUCT QUALITIES AND PROPERTIES

The products collected from the selected Beneficiation Experiments were analyzed for moisture, equilibrium moisture, and residuum contents. They are also evaluated for pore volume and pore size distribution, and assessed for stability towards self-heating.

Before the characterization of the products from these Beneficiation Experiments, an experiment was carried out to evaluate if the residuum was irreversibly bound to the coal during the process. The results of this experiments and product characterization are discussed below.

7.1 Bonding of Residuum to Coal

While the limitations in the pilot plant operation prohibit the correlation of residuum applied at the pump with the residuum content determined on the product, it is important to know if there is any irreversible bonding between the residuum and the coal after heat treatment. Known quantities of heat treated coal and residuum were mixed and the mixtures were subjected to soxhlet extraction. The residuum contents determined from soxhlet extraction are compared with the known quantity of residuum added in the mixtures. The determinations of irreversible bonding were conducted on the Obed and Highvale coals using the five different types of residuum.

The results of this study are shown in Table 18. Residuum contents determined by soxhlet extraction are comparable to the quantites added to the heat treated coal. Considering the experimental error of the soxhlet extraction method, these data indicate that irreversible bonding does not occur. Extraction of materials from coal is not likely to occur when methylene chloride of a boiling point of about 40°C was used in the soxhlet extraction.

Table 18 also provides the moisture contents of the samples. In all cases a negative moisture value was determined. This means that the sample gained weight while being dried at 107°C. This weight gain is attributed to sample oxidation which is further discussed in the following sections.

7.2 Residuum Contents of Products

Residuum contents of the products from the selected experiments are shown in Table 19. The values determined range from 2.5 wt% to 5.4 wt%, using the soxhlet extraction method.

Although it is impossible to compare the residuum contents determined with the amount of residuum applied, the data from thermogravimetric analysis and from the TGA Simulator suggest that negligible amounts of residuum were lost in the process, particularly when the treating drum was operated at the 250°C temperature range.

7.3 Product Moisture

Table 19 indicates that the products were essentially bone dry. This would be expected for coal heated to 350° C.

It is noteworthy that negative moisture values were also recorded for the product samples, but not to the same extent as they were for the samples used in the correlation of the soxhlet extraction method to the known asphalt addition rates (section 7.1). The only significant differences between the two sets of samples were:

1. The correlation samples were not as well coated as the test product samples because the latter were tumbled in the treating drum for about four minutes whereas the former were shaken for about one minute.

2. The correlation samples cooled down quickly whereas the test product samples remained hot for much longer.

Although the exact reason for the differences in moisture levels is not known, the significance is that the correlation samples were more reactive (increased in weight due to oxidation) than the test product samples. Since it was visually obvious that the product samples were coated better than the correlation

samples, it would seem that the residuum coating was preventing oxidation during the drying procedure.

7.4 Product Equilibrium Moisture

Table 19 and Figures 10 and 11 provide the equilibrium moisture values of the feed coals, of the heated coals without residuum, and of the treated products. Figure 12 shows the reduction in equilibrium moisture.

It is obvious from the results that a significant reduction in equilibrium moisture is achieved solely from heating the coals, particularly for the Highvale coal. These results agree with those achieved in previous projects.

With respect to the effect of treating drum oxygen content there does not appear to be a consistent effect for the Obed coal. For the Highvale coal it appears that high oxygen produces lower equilibrium moisture. However, the observed effect is probably due to residuum application rate and not to treating drum oxygen level. For each residuum, with the single exception of Cenex on Obed coal, the equilibrium moisture was always lower for the product with the higher amount of residuum, regardless of treating drum oxygen content.

Overall, the results suggest that there is no significant difference amongst the residua with respect to their effect on equilibrium moisture.

7.5 Pore Volume and Pore Size Distribution

Table 20 provides the data on pore volume and pore size distribution for micropores ($\leq 20\mathring{A}$), mesopores ($20 - 200\mathring{A}$), and macropores ($200\text{-}1000\mathring{A}$). Only selected products were analyzed, but the feed samples before and after heating to 350°C were included to provide additional information. Appendix 4 provides the full pore size distributions from which Table 20 was derived. It should be noted that pore structure determination by the BET Method has inherent limitations and is sensitive to the physical state of the samples. The trends of the results rather than absolute values, should be emphasized in data interpretation.

Similar trends in pore structures are observed for Obed and Highvale coals before and after thermal treatment. Heating the coals to 350°C increased the total pore volume and the proportion of macropores. The pore volumes of Obed and Highvale coals were increased from 650 to 731 (12.5% increase) and from 1,316 to 1,535 x 10^{-5} cc/g (16.6% increase), respectively. The proportion of macropores for Obed after heating was increased to 59.6% from 41.5%; whereas the increase in macropore distribution for Highvale was from 50.8% to 59.9%.

Data obtained on products from both coals show that the residuum treated products have lower pore volumes than the feed samples before and after heating. This supports the expectation that residuum plugs coal pores. The pore size distribution data shows that there is a decrease of macropores for the Obed products when compared to the heat treated product, for all residua except CANMET Demo Pitch. An increase of macropores was also observed for the Highvale products prepared from the CANMET Demo Pitch, the only products selected from the Highvale coals.

The residua appear to fall into three groups with respect to their effect on pore volume: The Koch and Cenex group, the Peace River and Suncor group, and CANMET Demo Pitch group. The trends that are evident in going from the first to the third group are:

- Total pore volume increases.
- The proportion of macro-pores increases with a corresponding decreases of micro-pores.

These three groupings are consistent with the physical properties of the residua (see Table 5). The Koch and Cenex have the lowest viscosities, densities and softening points as well as the highest penetrations. With respect to these properties, the Peace River and Suncor are intermediate to the Koch and Cenex and the CANMET Demo Pitch. The CANMET Demo Pitch is significantly different than the other residua, with respect to physical properties as well as effect on porosity.

The effect of oxygen level in the treating drum on pore structure of the products is revealled in a set of limited data. While there is no direct proof, it is suspected that the pore structures are dependent on carbon dioxide/nitrogen sorption by the products in the treating drum. Pore volumes determined on Obed products prepared from Peace River and CANMET Demo Pitch show that low oxygen atmosphere produces products of low pore volumes but little changes in pore size distributions. Since carbon dioxide was used to condition these products, this may suggest that carbon dioxide was irreversibly taken up by pores of all sizes, thus reducing the total pore volume but showing little effect on pore size distributions.

The results from Highvale coal products prepared from CANMET Demo Pitch give an opposite trend in total pore volume but essentially the same pore size distributions. In the conditioning of the Highvale products, a mixture of carbon dioxide and nitrogen was used. These data appears to suggest that there are very little sorption of nitrogen during the process of product stabilization.

It should be noted that the equilibrium moistures of the products do not agree with the pore volume trends. The heated products without residuum had significantly lower equilibrium moistures than the feed coals, yet the corresponding pore volumes increased. Also, for the Obed coal, the Koch and Cenex treated products had significantly lower pore volumes than the CANMET Demo Pitch products, yet the corresponding equilibrium moistures were either similar or even reversed. This appears to support that equilibrium moisture is highly dependent on the hydrophilic function groups which will be eliminated at high temperatures.

7.6 Product Stability

The results of the stability evaluations are provided in Table 21 and in Figure 13 to 20. The static isothermal oxygen absorption test used to evaluate stability is but one of many tests identified in the literature as being suitable for indicating the relative stability of coals.

This discussion will focus on the oxygen sorption and carbon monoxide production data. Since carbon dioxide (CO_2) was used in the low oxygen tests the

data of carbon dioxide production for these tests is impossible to interpret with confidence as the carbon dioxide measured in the head gas could come from either oxidation of the coal or from desorption of some of the carbon dioxide that was adsorbed during the experiments. One would anticipate that the carbon dioxide values would be greater for the tests that used carbon dioxide (low oxygen tests) than for the high oxygen tests. This is the case for the Highvale products and is true for the Obed coal products treated with the CANMET Demo Pitch. For the Obed products produced with Peace River and Cenex the carbon dioxide production values are lower for the tests that used carbon dioxide in the treating drum.

Figures 13 and 14 suggest that oxygen absorption increases as the amount of residuum on the coal increases. Since low oxygen absorption is desireable the results suggest that addition of residuum decreases stability. On the other hand, the CO production data plotted in Figures 15 and 16 indicate that CO production decreases as the amount of residuum increases, thereby suggesting that the addition of residuum increases stability.

With respect to coal stability, oxygen absorption is undesireable if the oxygen is reacting with the coal. Oxygen absorption is not necessarily a sign of instability if the oxygen remains on the coal surface. Thus, the conversion of oxygen to carbon monoxide and carbon dioxide is a more meaningful measure of coal's reactivity. On the basis of carbon monoxide produced to oxygen consumed, Figures 17 and 18 show that the residuum treated products are significantly less reactive than the heated coals untreated with residuum. Figures 19 and 20 show the ratio of carbon monoxide produced to oxygen adsorbed. On the other hand, relative to the moist feeds, all the products (residuum treated or untreated) are significantly more reactive.

With respect to the individual residua, it seems that CANMET Demo Pitch and Peace River produce the most stable products. For the Highvale coal only CANMET Demo Pitch applied under high oxygen conditions produced low oxygen absorption and CO production values, although for this product the ratio of CO produced to oxygen consumed was the highest of all the Highvale treated products. With the Obed coal, CANMET Demo Pitch at both high and low oxygen levels and Peace River at low oxygen levels gave the lowest oxygen absorption

values. The Peace River at low oxygen levels and CANMET Demo Pitch at high oxygen levels also gave the lowest CO production values. Considering both the Obed and Highvale results together, it appears that CANMET Demo Pitch applied in a high oxygen atmosphere produces the most stable products. It must be noted that this conclusion is based on a limited data base and that the variability in the residuum contents makes direct comparison difficult.

It should also be noted that the stability test method largely ignores the effect of moisture on stability, particularly the heat of wetting. It is reasonable to assume that the greater the gap between equilibrium moisture and product moisture, the greater is the potential heat generation due to the heat of wetting. Thus, the products with the lowest equilibrium moistures should be the least affected by moisture. The data presented indicates that there was no significant difference amongst the various residua with respect to their effect on equilibrium moisture, but that the addition of residuum reduced equilibrium moisture relative to no residuum.

8.0 CONCLUSIONS

The results of this research contract prove experimentally, that a wide range of petroleum residua are suitable for the Gulf Beneficiation Process. The findings of this study also offer a database for the selection of residuum for processes operated under similar conditions. The following can be concluded for this research contract.

1. The effect of a wide range of physical and chemical properties of residua on product qualities and properties appears to be minimal in Gulf's two stage beneficiation process.

2. There are no significant differences in product qualities and properties when different oxygen atmospheres are used in the treating stage.

3. Using static oxygen sorption and carbon monoxide production as the sole criterion for stability evaluation, the addition of residuum consistently lowers the carbon monoxide production of heated coal, although the oxygen sorption of residuum treated products is always higher. Since the production of carbon monoxide and carbon dioxide is indicative of the reactivity of a product, it can be inferred that the addition of residuum is beneficial in the stabilization of the product.

4. Pore volumes of residuum treated products are lower than the pore volumes of the feedstocks and of the feedstocks that received only thermal treatment. A shift in pore size distributions is also observed independent of oxygen atmosphere. Except for the CANMET Demo Pitch, all residua treated products decrease the proportion of macropores in the Obed products.

5. Pore volume and equilibrium moisture determinations are not consistent. Equilibrium moisture is reported to be affected by the presence of hydrophilic functional groups. This possibly explains

why the heat treated product shows lower equilibrium moisture value while it exhibits a higher pore volume than the feedstock without heat treatment.

6. Reactions in the TGA Simulator are surface restricted. Therefore, differences in weight loss are observed in high and low oxygen content experiments. Because of the restriction in surface reactions, the TGA Simulator and the conventional TGA do not produce the same results of weight loss in absolute terms.

7. The amounts of gases and condensable hydrocarbons generated when heating residua at 300°C in a TGA Simulator are insignificant. However, the nature of the species generated at different oxygen environments suggest different reaction mechanisms.

8. Reasonable correlations between the conventional TGA data and the initial boiling point and final weight loss from simulated distillation are observed, when these techniques are applied for the analysis of the residua.

9. There are no significant changes in the physical properties of the residua before treatments after heat treatment, and after coal beneficiation.

10. Carbon dioxide treatment of the upgraded products appears to be beneficial in lowering their oxygen sorption and carbon monoxide production. Additional stabilization may still be required such as reducing the gap between the equilibrium moisture and product moisture.

9.0 RECOMMENDATIONS

Stability of products generated from this research contract was solely assessed by a modified oxygen sorption method. To firmly establish the capability for the evaluation of product stability, additional methods should be developed and applied to products from low rank coal upgrading processes. The following are recommended:

1. Equilibrium moisture and pore volume are two product properties that should be useful in establishing the effect of the Gulf process on coals, yet these two properties follow opposite trends. The relationship between equilibrium moisture and pore volume should be critically defined.

2. Assess product stability by other methods preferably measuring a different property. The new technique developed recently for the crossing point method at CANMET should be investigated for Gulf products. Water sorption should also be followed for all the products.

3. Carbon dioxide cooling in conjuction with other stabilization options should be carefully examined. Bench scale experiments should be carried out on samples under carbon dioxide atmosphere. The stability of the carbon dioxide treated sample should be studied to provide supporting data.

4. Alternatives in controlling the exact quantity of residuum in the Gulf process in the pilot scale should be examined. This will eliminate all the uncertainty regarding product properties caused by variations in residuum contents of the products.

Table 1

SIZE DISTRIBUTIONS OF OBED AND HIGHVALE COALS

Size analysis of Obed coal head sample:

Size Fraction (mm)	Weight (%)	Cumulative Weight (%)
+12.50	10.3	10.3
12.50 x 6.70	33.4	43.7
6.70 x 3.35	26.6	70.3
3.35 x 1.70	17.4	87.7
1.70 x 0.60	8.4	96.1
0.60 x 0.30	1.6	97.7
0.30 x 0.15	1.2	98.9
-0.15	1.1	100.0

Size analysis of Highvale coal head sample:

Size Fraction (mm)	Weight (%)	Cumulative Weight (%)
+12.50	10.2	10.2
12.50 x 6.70	25.5	35.7
6.70 x 3.35	21.2	56.9
3.35 x 1.70	16.0	72.9
1.70 x 0.60	14.6	87.5
0.60 x 0.30	5.9	93.4
0.30 x 0.15	3.9	97.3
-0.15	2.7	100.0

Table 2

CHARACTERIZATION OF OBED AND HIGHVALE COALS

Obed: High Volatile C Bituminous

Total Moisture	:	15.1%
Equilibrium Moisture	:	12.3%
Calorific Value, cal/g d.b.	:	6215
Proximate Analysis, d.b.		
Ash	:	15.8%
Volatile Matter	:	37.8%
Fixed Carbon	:	46.4%
Ultimate Analysis, d.b.		
Ash	:	15.8%
Carbon	:	60.3%
Hydrogen	:	4.6%
Nitrogen	:	1.6%
Sulfur	:	0.1%
Oxygen	:	17.6%

Highvale: Subbituminous B

Total Moisture	:	20.1%
Equilibrium Moisture	:	19.7%
Calorific Value, cal/g d.b.	:	5440
Proximate Analysis, d.b.		
Ash	:	20.5%
Volatile Matter	:	32.8%
Fixed Carbon	:	46.7%
Ultimate Analysis, d.b.		
Ash	:	20.5%
Carbon	:	55.9%
Hydrogen	:	3.4%
Nitrogen	:	1.1%
Sulfur	:	0.1%
Oxygen	:	19.0%

Table 3

CHARACTERIZATION OF THE POROSITY OF OBED AND HIGHVALE COALS

	Obed	Highvale
Pore Volume, cc/g	0.00650	0.01316
Pore Size Distribution:		
Micro-pores (0-20Å), %	8.4	3.6
Meso-pores (20-200Å), %	50.1	45.6
Macro-pores (+200Å), %	41.5	50.8

Table 4

ANALYSIS OF RESIDUA USED FOR COAL BENEFICIATION

Residuum	Koch 85/100 Asphalt	Cenex PDA	Peace River D85-70	Suncor D84-96	CANMET Demo Pitch D86-115
H_2O%	0.0	0.0	0.0	0.0	0.0
Ash %	0.0	0.0	0.0	1.0	1.9
C%	86.3	83.8	81.2	81.3	86.3
H%	10.4	9.6	9.5	9.8	7.3
N%	0.8	0.7	0.8	0.6	1.3
S%	2.0	4.5	7.5	6.1	3.0
O% (By Difference)	0.5	1.4	1.0	2.2	2.1
H/C Mole Ratio	1.45	1.38	1.41	1.45	1.02
Calorific Value (Cal/gm)	10,160	9,820	9,690	9,720	9,290
Ni (ppm)	51.5	75.0	109.0	124.5	151.4
V (ppm)	67.5	200.0	309.0	336.3	365.3

Table 5

PHYSICAL PROPERTIES OF RESIDUA

Residuum	Koch 85/100 Asphalt	Cenex PDA	Peace River D85-70	Suncor D84-96	CANMET Demo Pitch D86-115
Softening pt (°C)	47	61	68.5	67.5	115
Penetration (at 25°C)	77	16	7	7.5	1
Density (g/ml at 15.6°C)	1.02	1.05	1.06	1.06	1.13
Viscosity (cps)					
at 150°C	114	577	667	687	2,930
at 200°C	25	77	90	94	118

Table 6

MOLECULAR WEIGHT AND SIMULATED DISTILLATION OF RESIDUA

Residuum	M.W (g/Mol)	Initial Boiling Point (°C)	Wt.% Remaining at 525°C End Point
Koch	930	455	96.9
Cenex PDA	1,024	364	93.1
Peace River	1,206	413	93.7
Suncor	1,017	391	92.9
CANMET Demo	861	388	96.6

Table 7

TGA ANALYSIS OF RESIDUA

	Wt% Remaining at Temperature (°C)					
	High Oxygen (200 ml/min Air)			Low Oxygen 150/N2 + 50/Air		
	200	300	350	200	300	350
Koch	99.7	96.9	86.3	99.9	98.3	91.4
Cenex PDA	100.1	93.7	83.6	100.1	93.4	84.8
Peace River	100.6	96.1	85.7	100.9	95.9	86.7
Suncor	99.9	95.3	85.0	100.0	96.4	88.0
CANMET Demo	99.4	96.8	90.7	100.4	97.0	90.5

Table 8

IATROSCAN ANALYSIS OF RESIDUA

Sample	Saturates	Aromatics 1	Aromatics 2	Polar A	Polar B
	Normalized Weight Percents				
Koch 85/100	20.8	7.8	31.3	21.5	18.6
Cenex PDA	15.3	6.2	31.6	23.8	23.1
Peace River	8.2	3.8	26.6	28.9	32.5
Suncor	10.3	4.4	27.9	27.8	29.6
CANMET Demo	12.3	1.7	40.5	20.2	25.3

Table 9

SIMULATED TGA ANALYSIS OF KOCH 85/100 RESIDUUM

EXPERIMENTAL OBSERVATIONS

Time (min)	Sample Temperature (°C)	% Weight Loss in 5% Oxygen	% Weight Loss in 21% Oxygen
0	130	---	---
5	190	0.03	---
10	240	0.26	0.22
20	260	1.14	1.84
30	280	1.52	2.29
40	300	1.62	2.31
50	300	1.64	2.33
60	300	1.66	2.33

Table 10

SIMULATED TGA ANALYSIS OF CENEX PDA RESIDUUM

EXPERIMENTAL OBSERVATIONS

Time (min)	Sample Temperature (°C)	% Weight Loss in 5% Oxygen	% Weight Loss in 21% Oxygen
0	130	---	---
5	190	---	---
10	240	0.04	0.14
20	260	0.42	0.84
30	280	0.45	0.94
40	300	0.50	0.96
50	300	0.52	1.00
60	300	0.52	1.02

Table 11

SIMULATED TGA ANALYSIS OF PEACE RIVER RESIDUUM

EXPERIMENTAL OBSERVATIONS

Time (min)	Sample Temperature (°C)	% Weight Loss in 5% Oxygen	% Weight Loss in 21% Oxygen
0	130	---	---
5	190	---	---
10	240	---	---
20	260	0.13	0.14
30	280	0.29	0.27
40	300	0.32	0.32
50	300	0.34	0.36
60	300	0.35	0.38

Table 12

SIMULATED TGA ANALYSIS OF SUNCOR RESIDUUM

EXPERIMENTAL OBSERVATIONS

Time (min)	Sample Temperature (°C)	% Weight Loss in 5% Oxygen	% Weight Loss in 21% Oxygen
0	130	---	---
5	190	---	---
10	240	---	---
20	260	0.08	0.22
30	280	0.18	0.54
40	300	0.26	0.60
50	300	0.46	0.62
60	300	0.50	0.64

Table 13

SIMULATED TGA ANALYSIS OF CANMET DEMO PITCH

EXPERIMENTAL OBSERVATIONS

Time (min)	Sample Temperature (°C)	% Weight Loss in 5% Oxygen	% Weight Loss in 21% Oxygen
0	130	---	---
5	190	---	---
10	240	---	---
20	260	---	---
30	280	0.02	0.02
40	300	0.02	0.04
50	300	0.06	0.10
60	300	0.06	0.14

Table 14

COMPARISON OF % WEIGHT LOSS FROM CONVENTIONAL TGA AND TGA SIMULATOR AT 300°C

Residuum	High Oxygen		Low Oxygen	
	TGA	TGA Simulator	TGA	TGA Simulator
Koch 85/100	3.1	2.31	1.7	1.62
Cenex PDA	6.3	0.96	6.6	0.50
Peace River	3.9	0.32	4.1	0.32
Suncor	4.7	0.60	3.6	0.26
CANMET Demo	3.2	0.04	3.0	0.02

Table 15

COMPARISON OF PHYSICAL PROPERTIES OF RESIDUA

(VIRGIN, HEAT TREATED, AND EXTRACTED AFTER COAL BENEFICIATION)

Residua	Treatment	Softening Point °C	Penetration Value 25°C
Koch 85/100	Virgin	47.0	77.0
	Heat treated at 300°C/5% Oxygen	44.0	88.0
	Heat treated at 300°C/21% Oxygen	44.5	86.0
	Low oxygen coated on coal	51.0	36.0
	High oxygen coated on coal	49.0	44.0
Cenex PDA	Virgin	61.0	16.0
	Heat treated at 300°C/5% Oxygen	61.5	14.5
	Heat treated at 300°C/21% Oxygen	61.5	14.5
	Low oxygen coated on coal	70.0	10.0
	High oxygen coated on coal	69.0	11.0
Peace River	Virgin	68.5	7.0
	Heat treated at 300°C/5% Oxygen	62.0	15.0
	Heat treated at 300°C/21% Oxygen	62.5	12.0
	Low oxygen coated on coal	68.5	9.0
	High oxygen coated on coal	67.0	12.5
Suncor	Virgin	67.5	7.5
	Heat treated at 300°C/5% Oxygen	61.5	13.0
	Heat treated at 300°C/21% Oxygen	62.0	12.0
	Low oxygen coated on coal	70.0	12.5
	High oxygen coated on coal	70.5	8.5
CANMET Demo	Virgin	115.0	1.0
	Heat treated at 300°C/5% Oxygen	115.0	0.5
	Heat treated at 300°C/21% Oxygen	115.5	0.0
	Low oxygen coated on coal	101.0	0.5
	High oxygen coated on coal	98.0	1.0

Table 16

COMPARISON OF RESIDUUM CONTENT DETERMINED BY "LARGE SCALE" EXTRACTION AND SOXHLET EXTRACTION

Product	% Residuum (Extraction) (500 g samples)	% Residuum (Soxhlet) (4 - 5 g samples)
Koch		
High O_2	3.7	4.9
Low O_2	3.0	4.5
Cenex		
High O_2	4.0	4.8
Low O_2	4.9	5.1
Peace River		
High O_2	3.1	3.7
Low O_2	3.0	4.0
Suncor		
High O_2	3.1	2.8
Low O_2	3.6	3.2
CANMET Demo		
High O_2	1.9	2.5
Low O_2	3.0	3.9

Table 17

TEST CONDITIONS*

Test No.	Test Variables			Test Data						Product Rate g/min
	Coal	Residuum	Oxygen Level	Minimum Oxygen Level, %	Residuum Level %	Temperatures, °C T_1	T_2	T_3	T_g	
1	Obed	Koch	High	--	4.9	345	240	120	100	255
2	Obed	Koch	Low	1.9	4.5	345	245	95	100	273
3	Obed	Cenex	High	--	4.8	350	250	140	--	302
4	Obed	Cenex	Low	3.0	5.1	350	250	140	--	255
5	Obed	Peace R.	High	--	3.7	340	270	130	120	252
6	Obed	Peace R.	Low	1.5	4.0	320	275	150	150	335
7	Obed	Suncor	High	--	2.8	340	270	130	130	246
8	Obed	Suncor	Low	4.2	3.2	350	275	70	135	248
9	Obed	CANMET	High	--	3.9	350	290	160	150	368
10	Obed	CANMET	Low	1.5	3.9	345	260	125	130	347
11	Highvale	Koch	High	--	4.5	360	270	140	125	326
12	Highvale	Koch	Low	2.0	4.2	365	265	125	125	342
13	Highvale	Cenex	High	--	5.1	370	260	110	100	256
14	Highvale	Cenex	Low	3.1	3.7	330	245	110	75	309
15	Highvale	Peace R.	High	--	5.1	360	300	160	150	336
16	Highvale	Peace R.	Low	0.9	4.2	320	285	110	120	365
17	Highvale	Suncor	High	--	3.5	380	295	155	160	227
18	Highvale	Suncor	Low	2.3	2.6	380	250	100	145	225
19	Highvale	CANMET	High	--	2.8	345	280	175	150	353
20	Highvale	CANMET	Low	0.4	5.4	370	265	80	110	204

Table 17
TEST CONDITIONS
continued

* Test No.'s are not the order in which the tests were done.

Minimum Oxygen Level = The minimum oxygen level recorded at the location corresponding to the minimumm of the oxygen concentration profile (Figure 2).

T_1 Temperature of coal exiting heating drum

T_2 Temperature of coal entering treating drum

T_3 Temperature of coal exiting treating drum

T_g Temperature of air/gases at mid-point of treating drum

Test 6, 10, 16 used CO_2 only to displace oxygen. All other low oxygen tests used a combination of CO_2 and N_2.

Table 18

RESIDUUM CONTENT DETERMINED BY SOXHLET EXTRACTION VS ACTUAL RESIDUUM CONTENT

Residuum	Coal	Residuum Content			Sample Moisture Content %
		From Wt. Added %	From Soxhlet Extraction %	Error %	
Koch	Obed	2.26	2.94	+23.1	-0.39
	Highvale	2.64	2.82	+6.8	-0.26
Cenex	Obed	n.d.	n.d.	--	n.d.
	Highvale	2.51	2.65	+5.6	-0.18
Peace River	Obed	3.21	2.63	-18.1	-0.54
	Highvale	2.00	1.85	-7.5	-0.40
Suncor	Obed	2.65	3.12	+17.7	-0.17
	Highvale	2.00	1.55	-22.5	-0.38
CANMET Demo	Obed	4.15	4.01	-3.4	-0.32
	Highvale	5.77	5.03	-12.8	-0.55

Table 19

PRODUCT CHARACTERIZATION

No.	Test Variables			Product Analyses		
	Coal	Residuum	Oxygen Level	Total Moisture %	Residuum Content %	Equilibrium Moisture %
1	Obed	Koch	High	-0.1	4.9	5.2
2	Obed	Koch	Low	0.0	4.5	6.0
3	Obed	Cenex	High	0.1	4.8	6.1
4	Obed	Cenex	Low	0.1	5.1	6.8
5	Obed	Peace R.	High	0.0	3.7	5.5
6	Obed	Peace R.	Low	-0.1	4.0	5.4
7	Obed	Suncor	High	-0.1	2.8	6.0
8	Obed	Suncor	Low	-0.2	3.2	6.0
9	Obed	CANMET	High	-0.4	3.9	5.6
10	Obed	CANMET	Low	-0.4	3.9	5.6
11	Highvale	Koch	High	0.0	4.5	11.6
12	Highvale	Koch	Low	0.1	4.2	12.2
13	Highvale	Cenex	High	0.3	5.1	12.5
14	Highvale	Cenex	Low	0.3	3.7	12.9
15	Highvale	Peace R.	High	0.0	5.1	11.1
16	Highvale	Peace R.	Low	0.1	4.2	11.5
17	Highvale	Suncor	High	-0.1	3.5	11.0
18	Highvale	Suncor	Low	-0.1	2.6	11.3
19	Highvale	CANMET	High	0.0	2.8	13.0
20	Highvale	CANMET	Low	0.0	5.4	10.4
	Obed	Feed		15.1	---	12.3
	Obed	350°C	Treated	---	---	8.2
	Highvale	Feed		20.1	---	19.7
	Highvale	350°C	Treated	---	---	12.3

Table 20

PORE VOLUMES AND PORE DISTRIBUTIONS FOR SELECTED PRODUCTS

Test Variables			Pore* Volume	Residuum Level	Pore Distribution, %		
Coal	Residuum	Oxygen Level	cc/g x 10^{-5}	%	Micro 0-20Å	Meso 20-200Å	Macro 200-1000Å
Obed	Feed		650		8.4	50.1	41.5
Obed	350°C	Untreated	731		3.5	36.9	59.6
Obed	Koch	Low	108	4.5	9.9	50.9	39.2
Obed	Cenex	Low	107	5.1	10.2	53.0	36.8
Obed	Peace R.	High	232	3.7	6.7	40.8	52.5
Obed	Peace R.	Low	123	4.0	8.3	40.6	51.1
Obed	Suncor	Low	201	3.2	6.9	39.5	53.6
Obed	CANMET	High	400	3.9	3.8	29.0	67.2
Obed	CANMET	Low	274	3.9	4.3	22.1	73.6
Highvale	Feed		1,316		3.6	45.6	50.8
Highvale	350°C	Untreated	1,535		6.1	34.0	59.9
Highvale	CANMET	High	974	2.8	2.3	27.5	70.2
Highvale	CANMET	Low	1,368	5.4	1.8	30.6	67.6

*The data refers only to pores of less than 1,000Å in diameter.

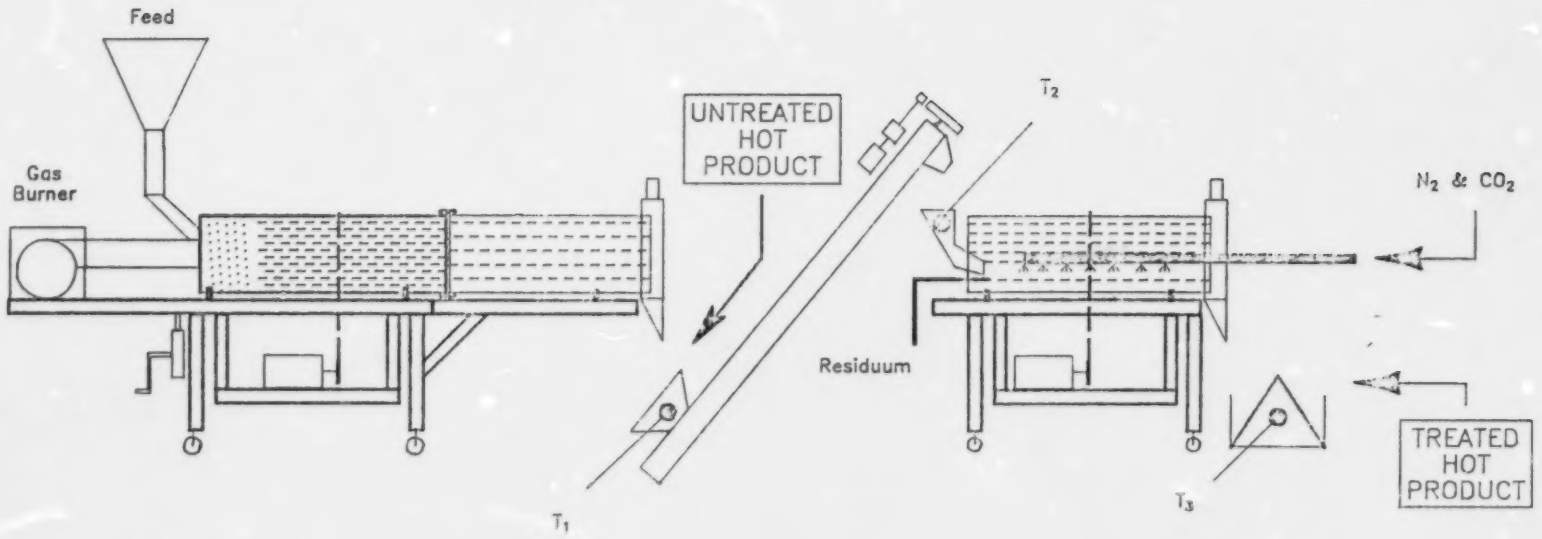
Table 21

PRODUCT STABILITY

No.	Test Variables			Stability Data		
	Coal	Residuum	Oxygen Level	Oxygen Sorption	CO Production	CO_2 Production
				ml/100g coal	ppm in head gas	ppm in head gas
	Obed	Feed		81	4	517
	Obed	350°C	Untreated	87	1946	2067
1	Obed	Koch	High	--	--	--
2	Obed	Koch	Low	205	1038	2011
3	Obed	Cenex	High	124	807	2683
4	Obed	Cenex	Low	233	2714	1444
5	Obed	Peace R.	High	135	796	2342
6	Obed	Peace R.	Low	79	445	1062
7	Obed	Suncor	High	--	--	--
8	Obed	Suncor	Low	155	1841	6434
9	Obed	CANMET	High	87	615	2213
10	Obed	CANMET	Low	74	1007	2427
	Highvale	Feed		65	3	4562
	Highvale	350°C	Untreated	124	3694	3522
11	Highvale	Koch	High	--	--	--
12	Highvale	Koch	Low	196	1497	863
13	Highvale	Cenex	High	--	--	--
14	Highvale	Cenex	Low	180	1431	1179
15	Highvale	Peace R.	High	199	1458	849
16	Highvale	Peace R.	Low	161	1538	3789
17	Highvale	Suncor	High	--	--	--
18	Highvale	Suncor	Low	245	2107	2334
19	Highvale	CANMET	High	70	827	2060
20	Highvale	CANMET	Low	269	1725	4881

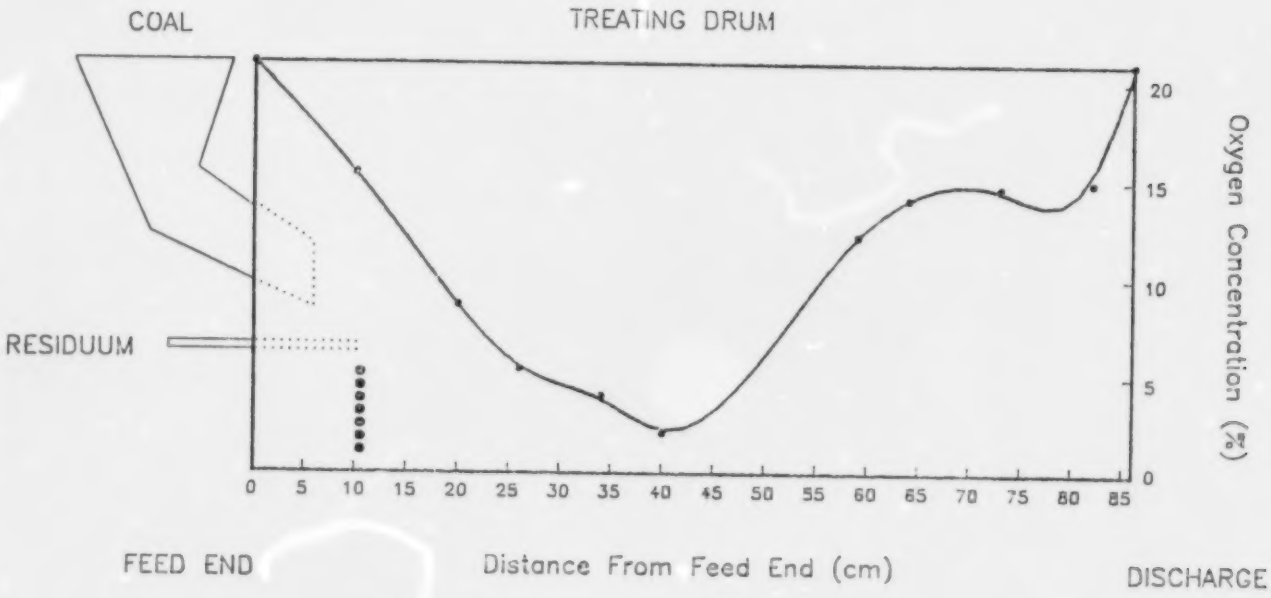
FIGURE 1

TWO–STAGE PROCESS SCHEME



HEATING DRUM → TRANSFER AUGER → TREATING DRUM → PRODUCT

FIGURE 2: Typical Oxygen Concentration Profile in Treating Drum During Low Oxygen Content Tests


COAL
TREATING DRUM
RESIDUUM
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85
0 5 10 15 20
Oxygen Concentration (%)
FEED END
Distance From Feed End (cm)
DISCHARGE

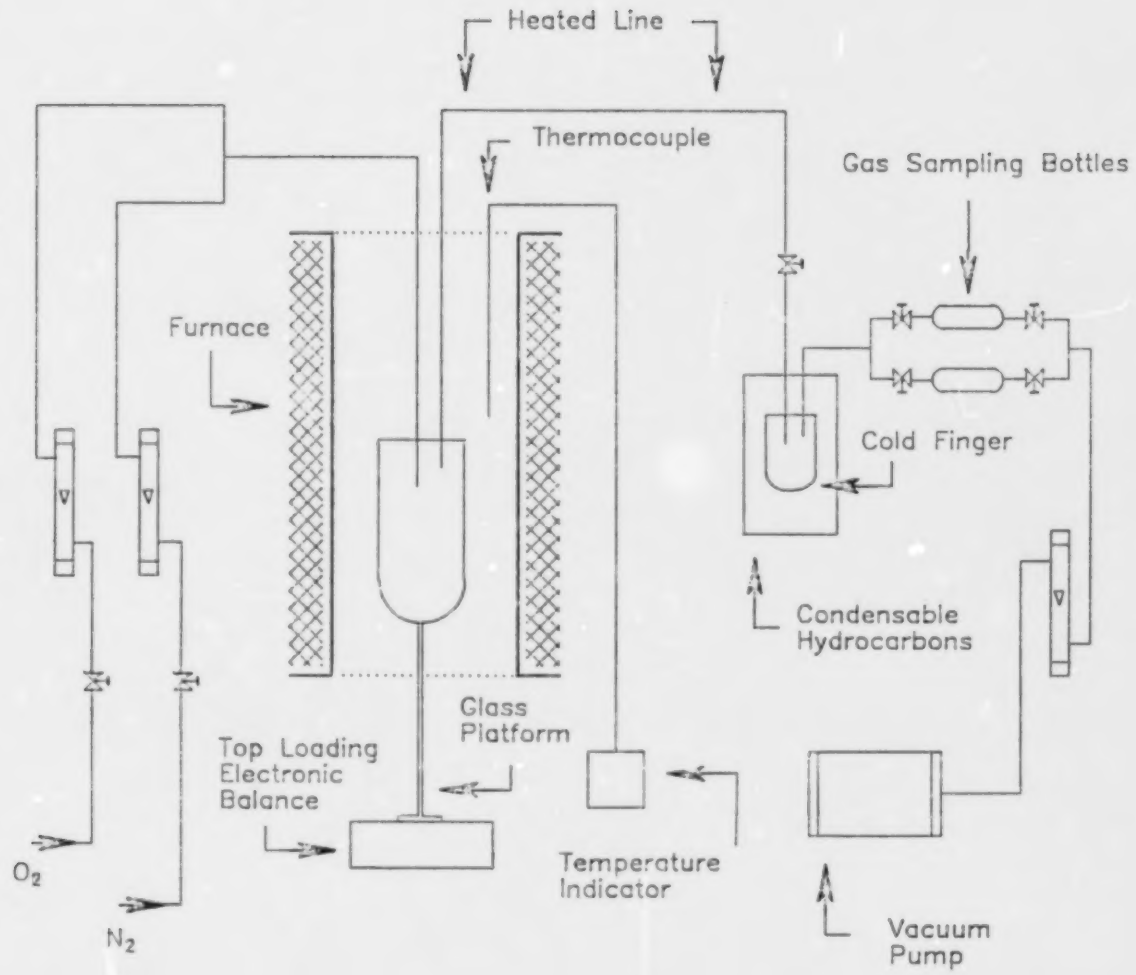


Figure 3:
SCHEMATIC FLOW DIAGRAM OF SIMULATED THERMOGRAVIMETRIC ANALYSER SYSTEM

FIGURE 4:
AVERAGE TGA WT. LOSS (300°C) AS A FUNCTION OF
INITIAL BOILING POINT (SIMULATED DISTILLATION)

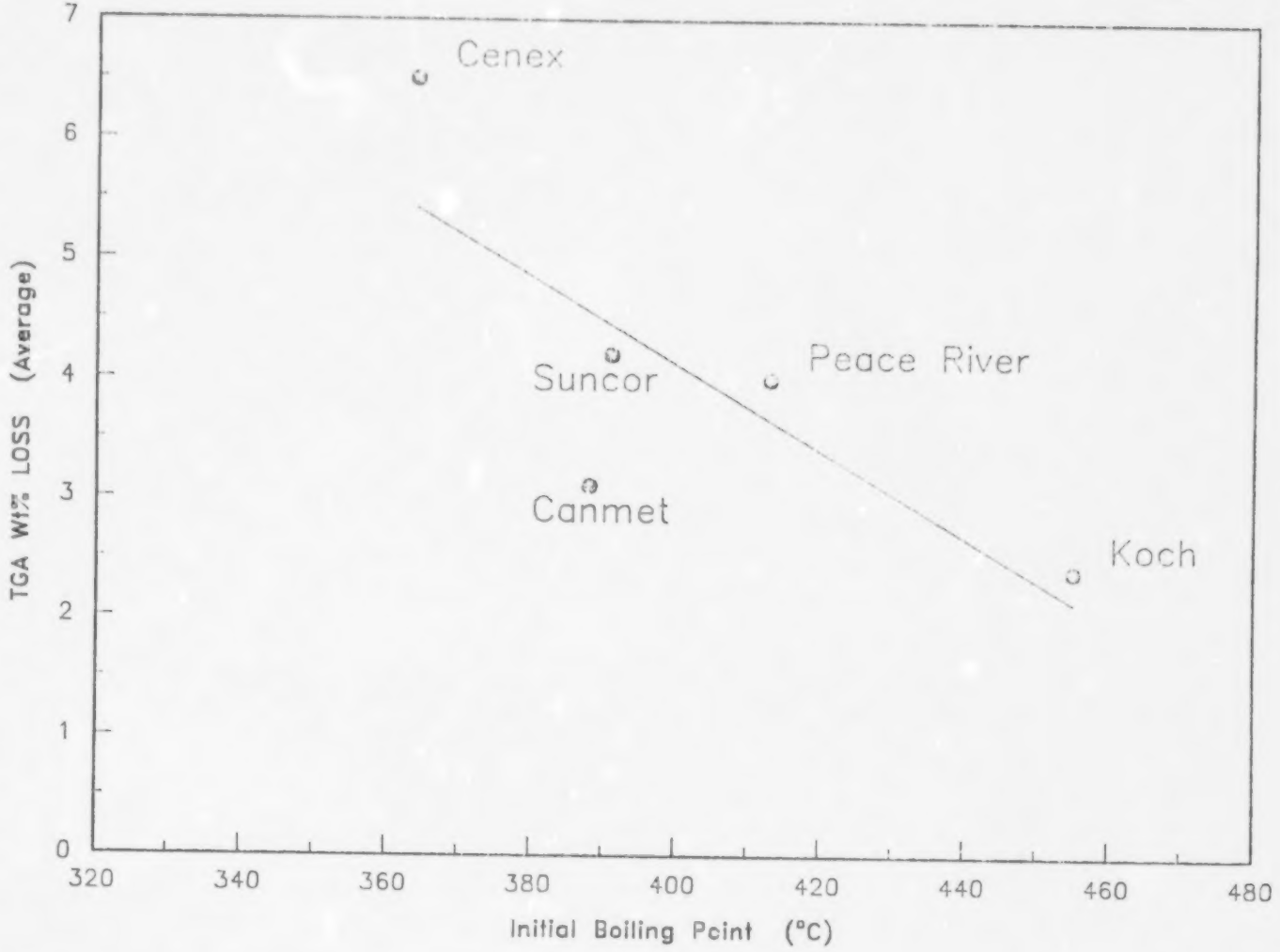


FIGURE 5:
AVERAGE TGA WT. LOSS (300°C) AS A FUNCTION OF
WEIGHT LOSS AT 525°C END POINT (SIMULATED DISTILLATION)

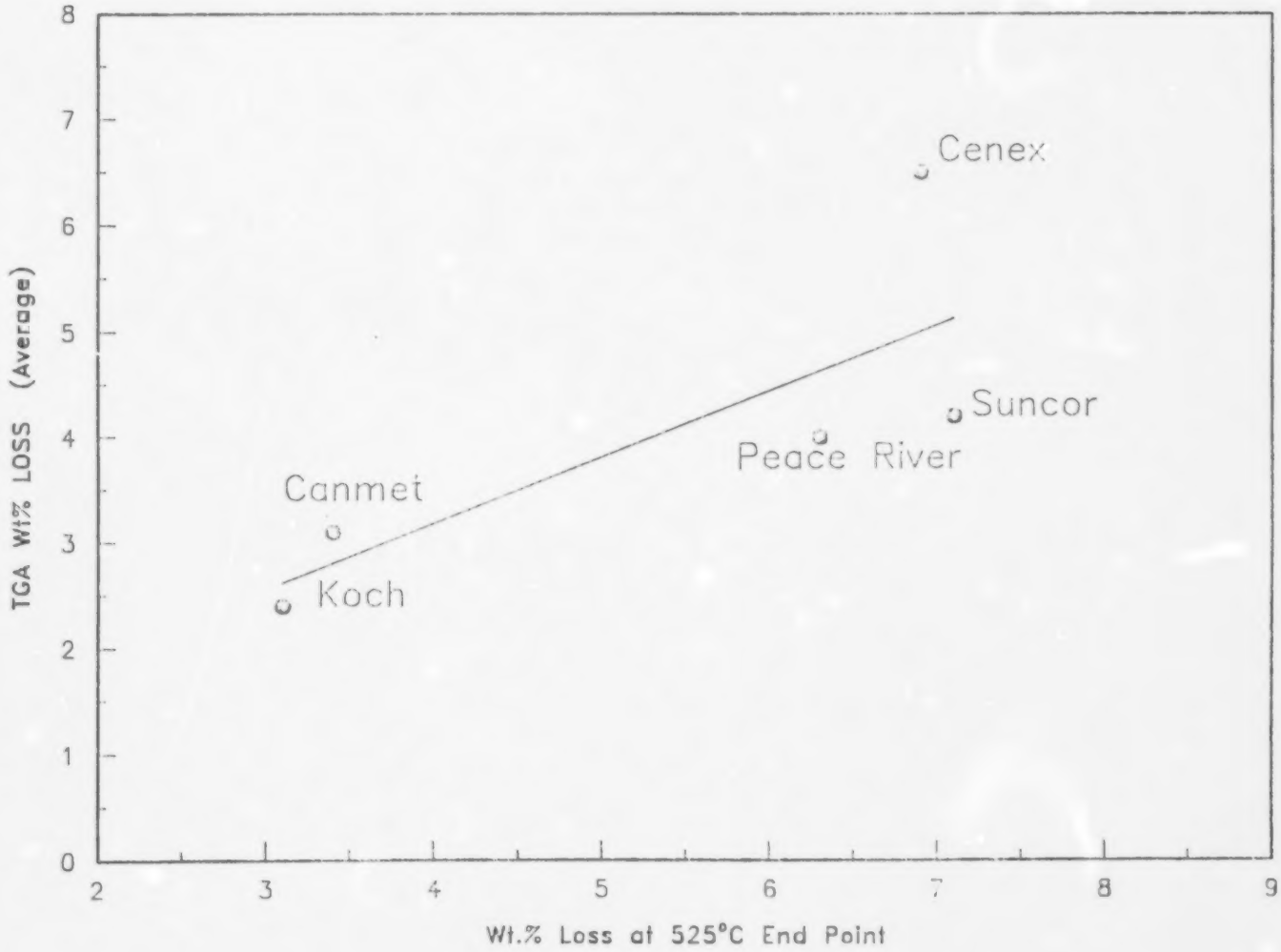


FIGURE 6:

BREAKDOWN OF COMPONENTS OF VARIOUS RESIDUUMS

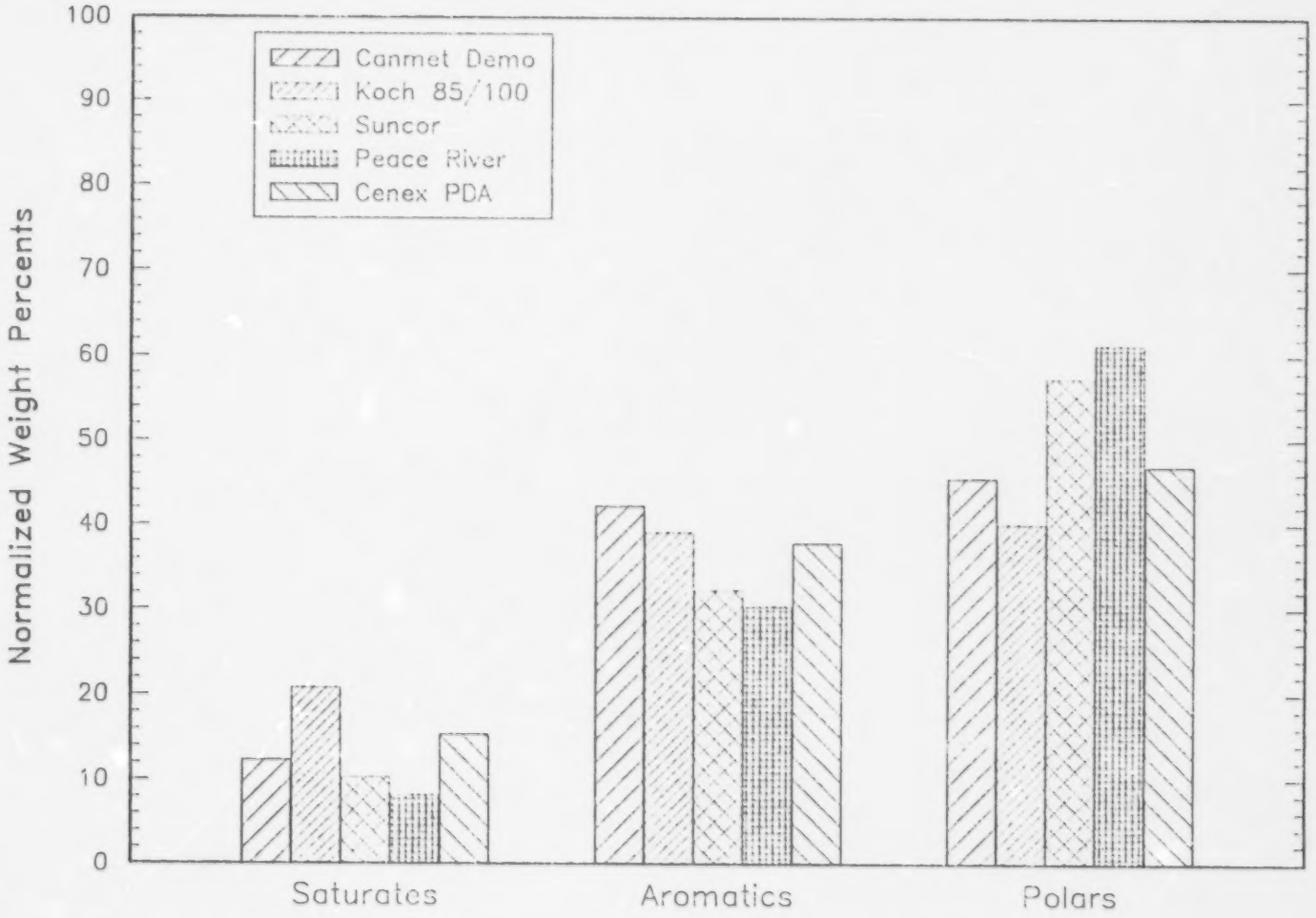


FIGURE 7:
RISE OF FURNACE TEMPERATURE WITH TIME
AT DIFFERENT FURNACE CONTROL SETTINGS

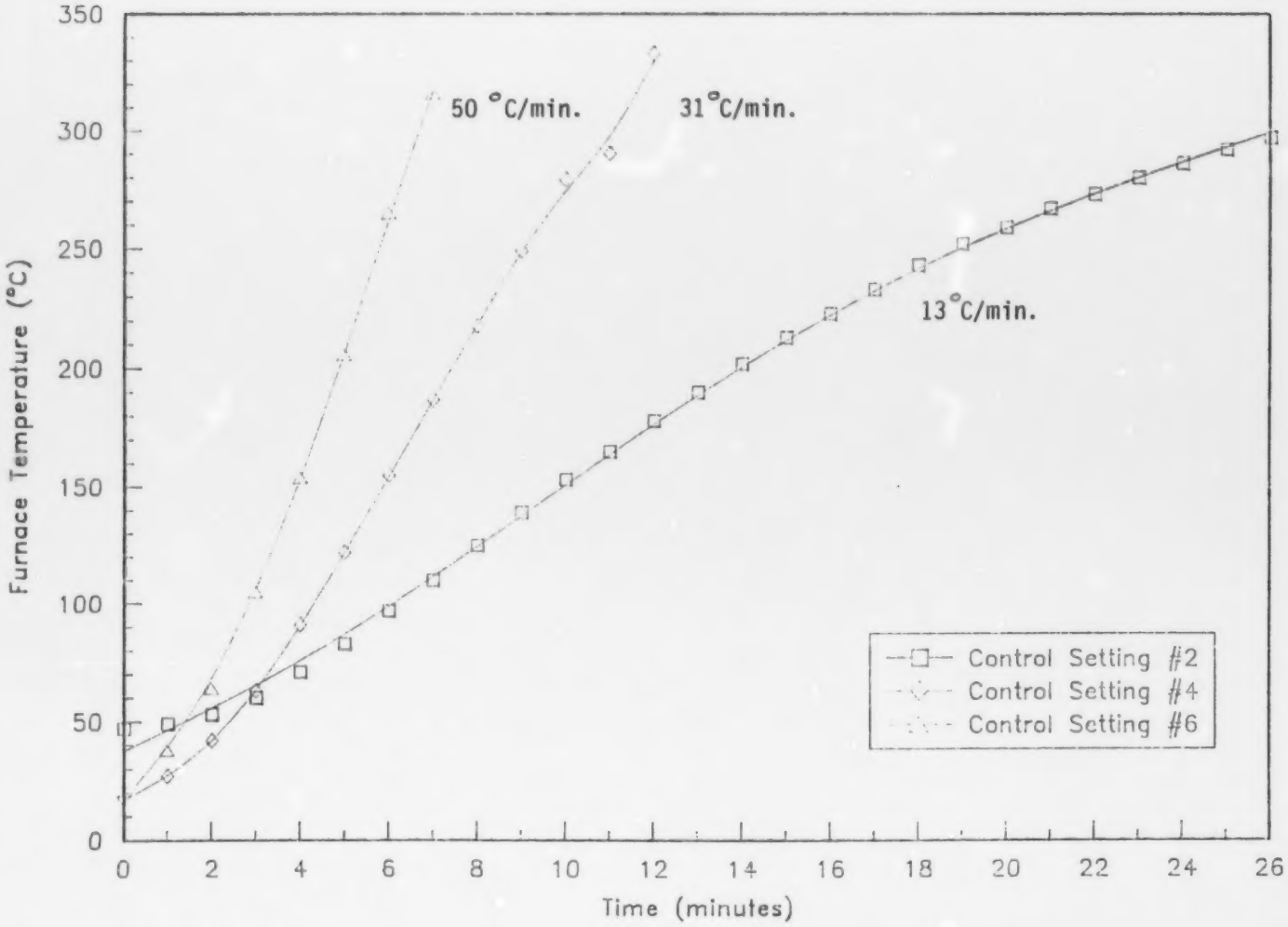


FIGURE 8:
RELATIONSHIP BETWEEN FURNACE TEMPERATURE
AND CENEX ASPHALT TEMPERATURE

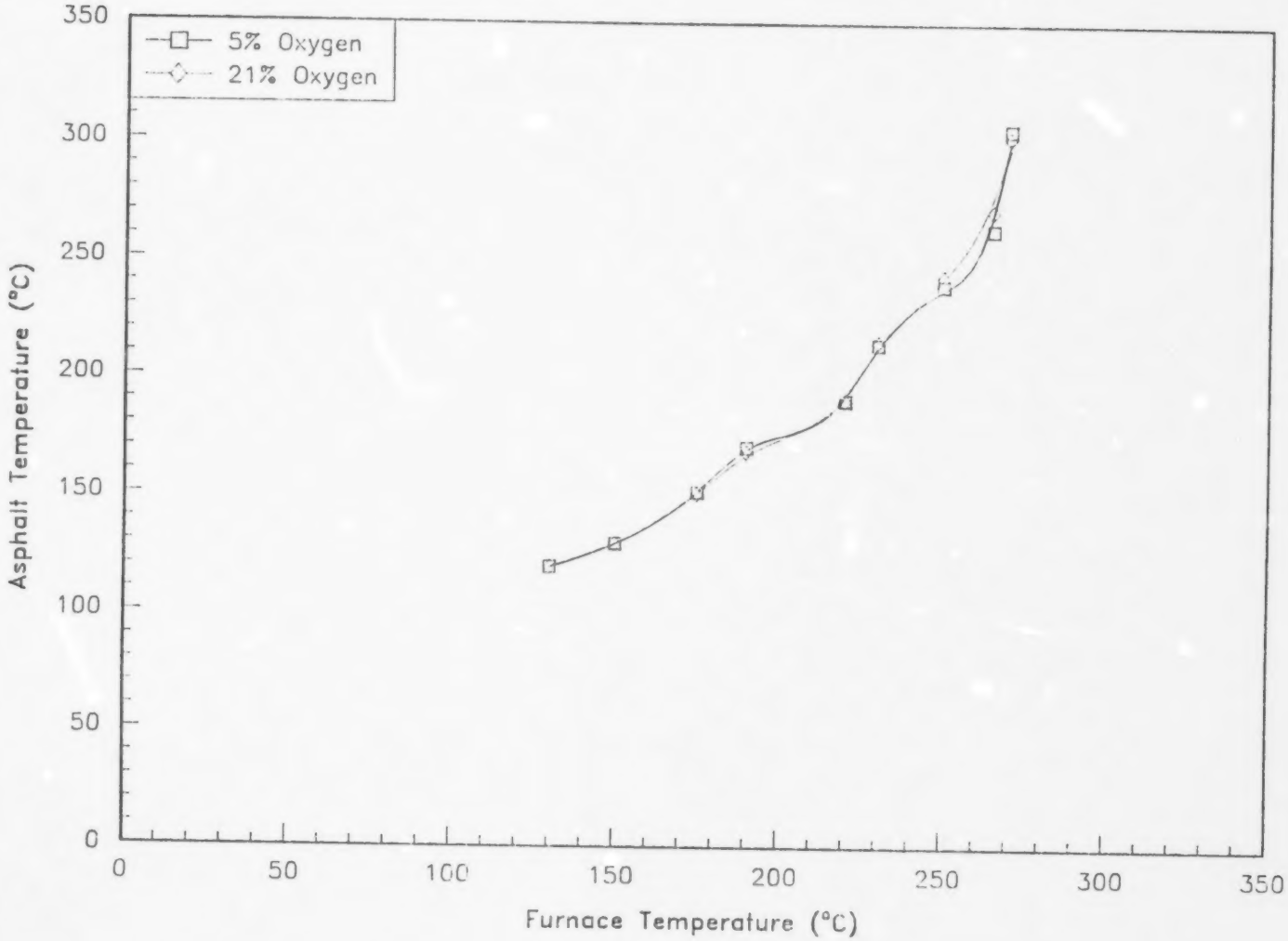


FIGURE 9
COMPARISON OF CONVENTIONAL TGA AND TGA SIMULATOR

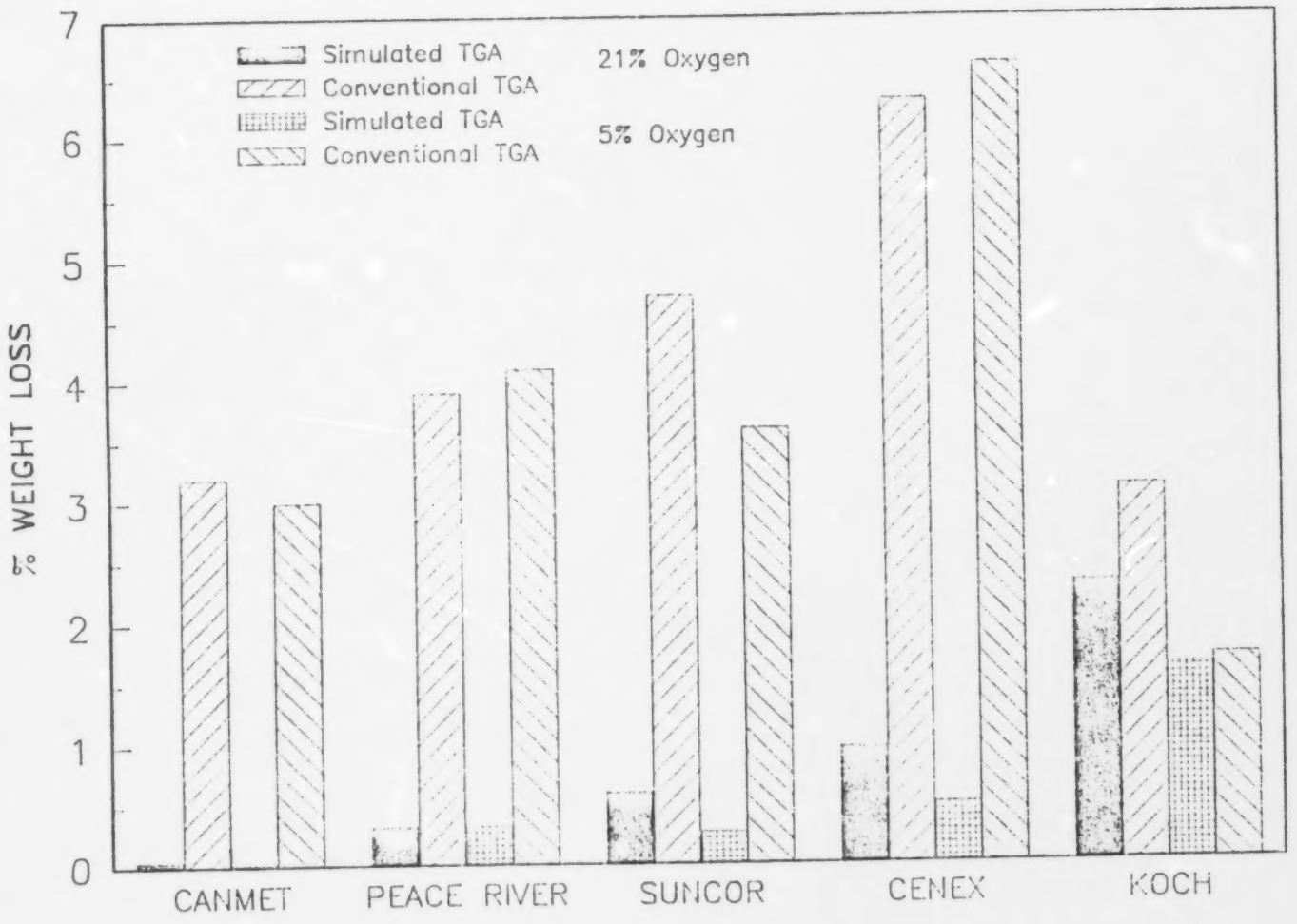


FIGURE 10:
EQUILIBRIUM MOISTURES OF OBED PRODUCTS

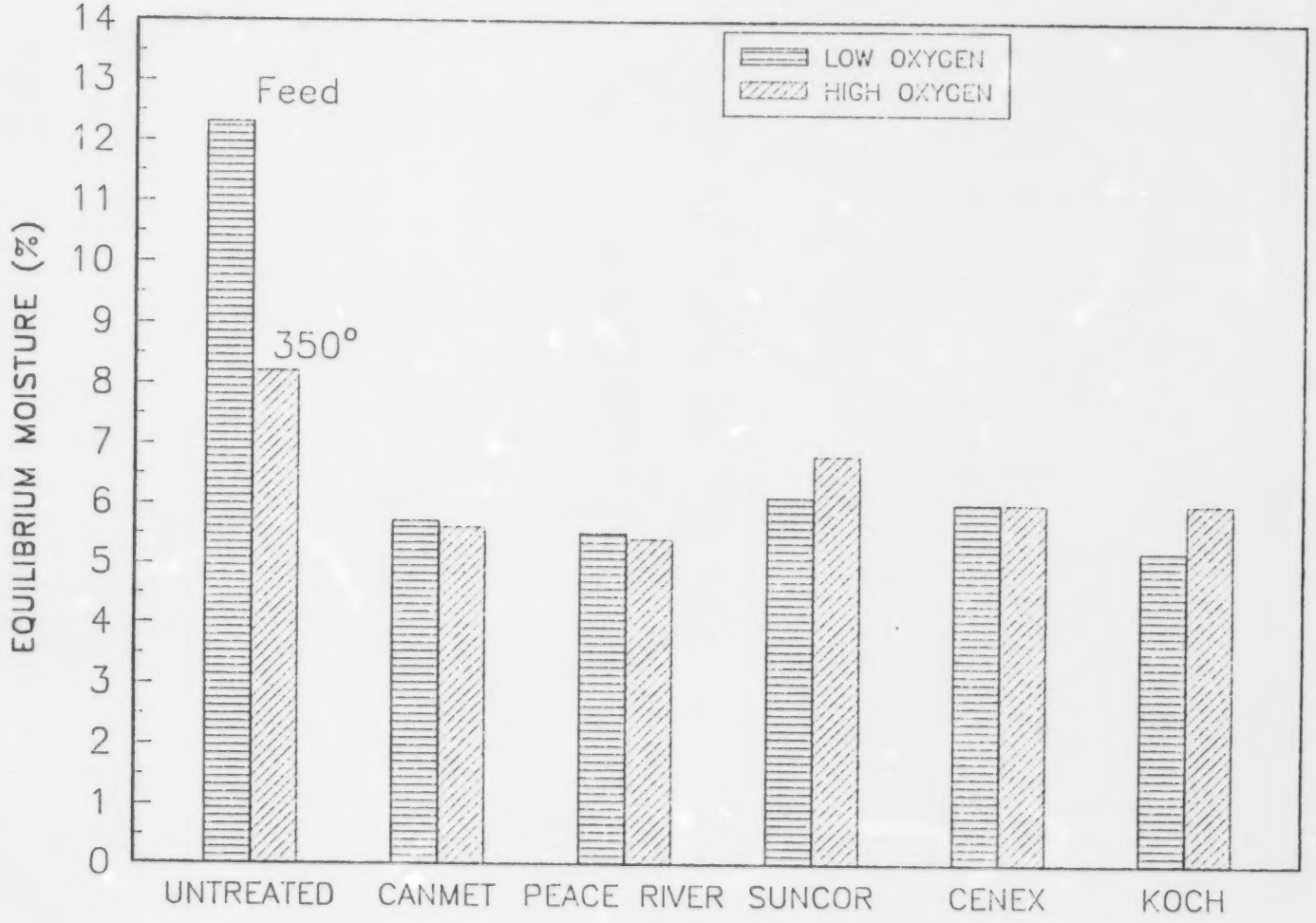


FIGURE 11
EQUILIBRIUM MOISTURES OF HIGHVALE PRODUCTS

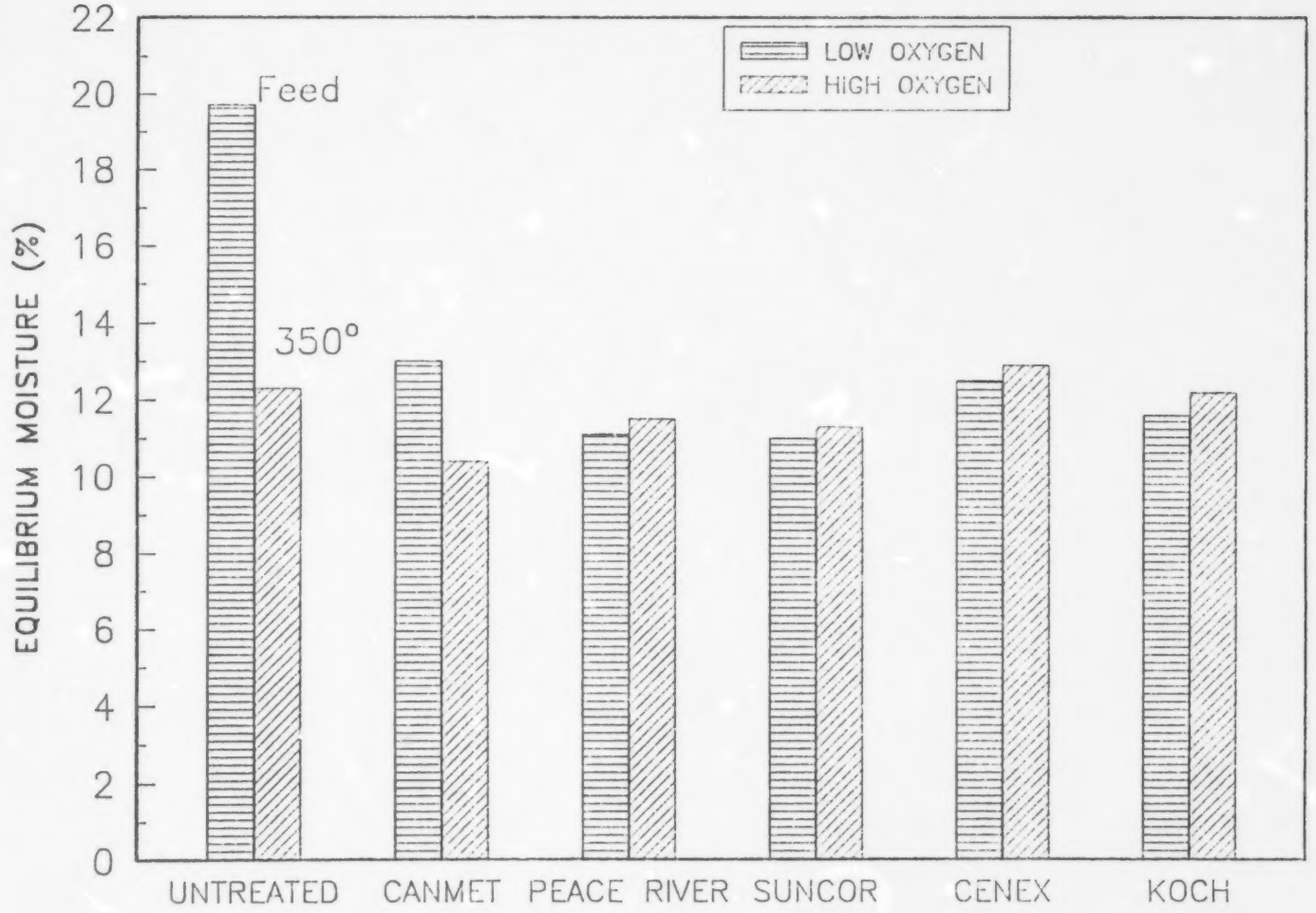


FIGURE 12:
REDUCTION IN EQUILIBRIUM MOISTURES OFOBED AND HIGHVALE COALS
TREATED UNDER BOTH LOW AND HIGH OXYGEN ATMOSPHERES

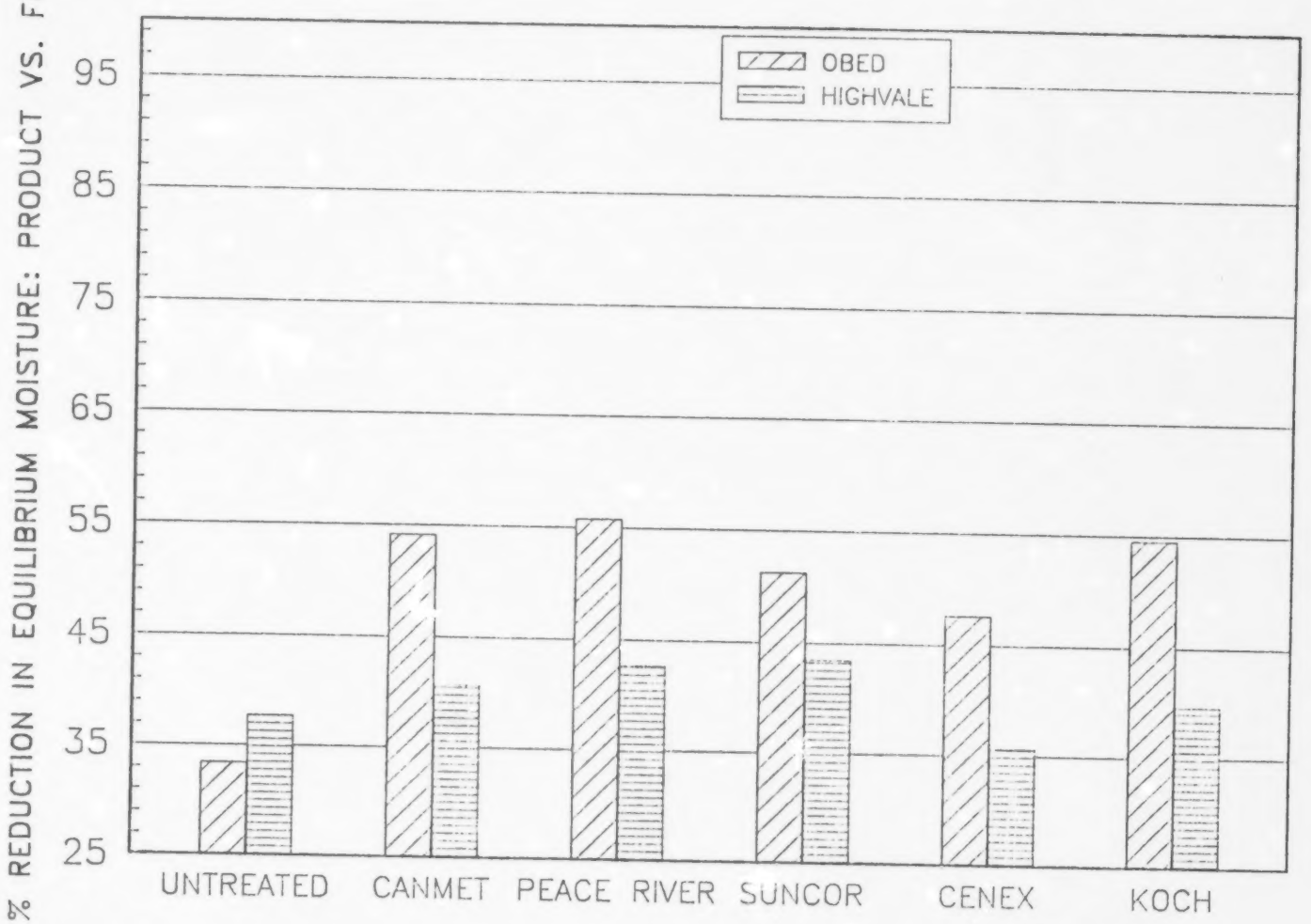


FIGURE 13:

OXYGEN ABSORPTION FOR OBED COAL
USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

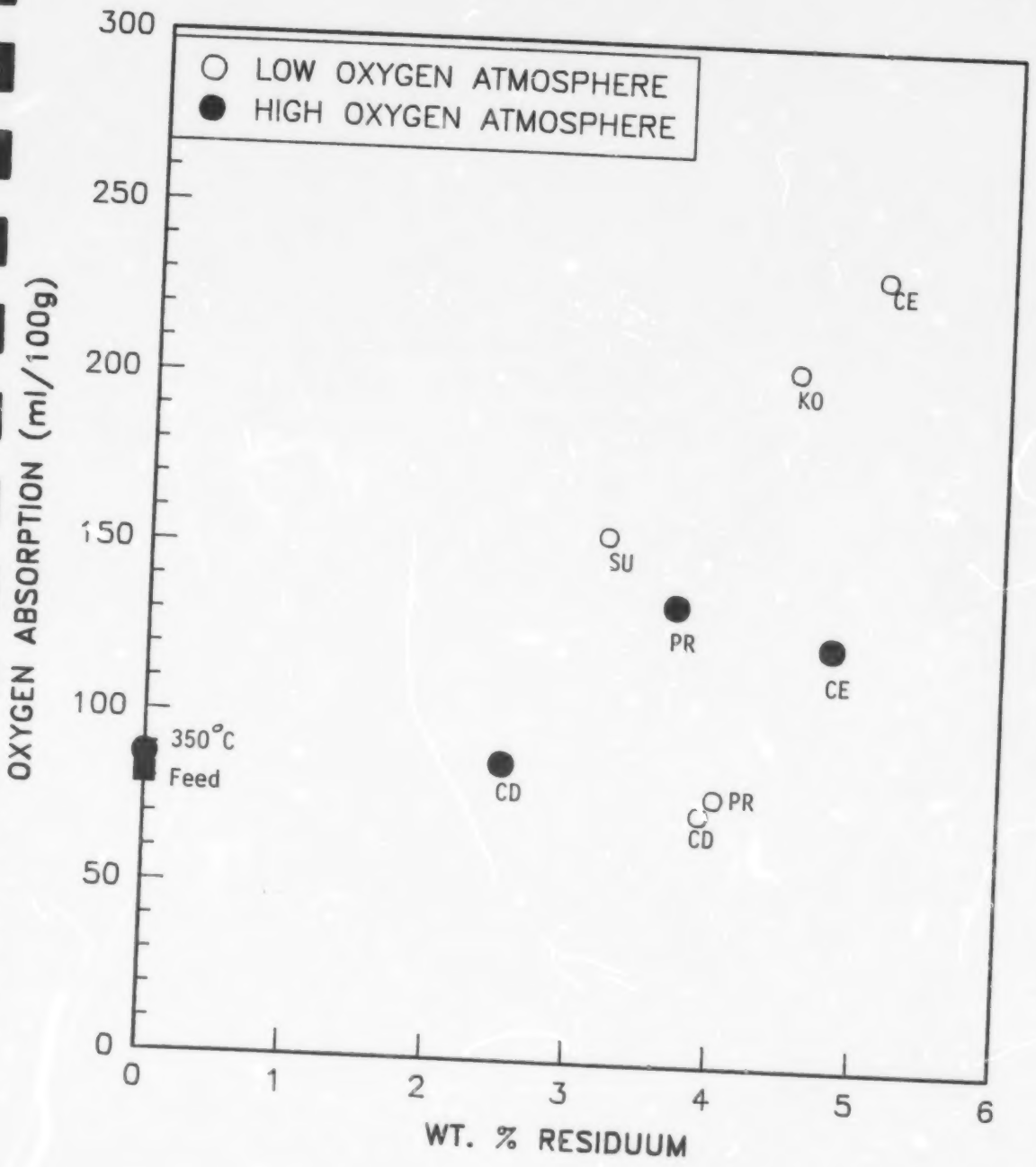


FIGURE 14:

OXYGEN ABSORPTION FOR HIGHVALE COAL USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

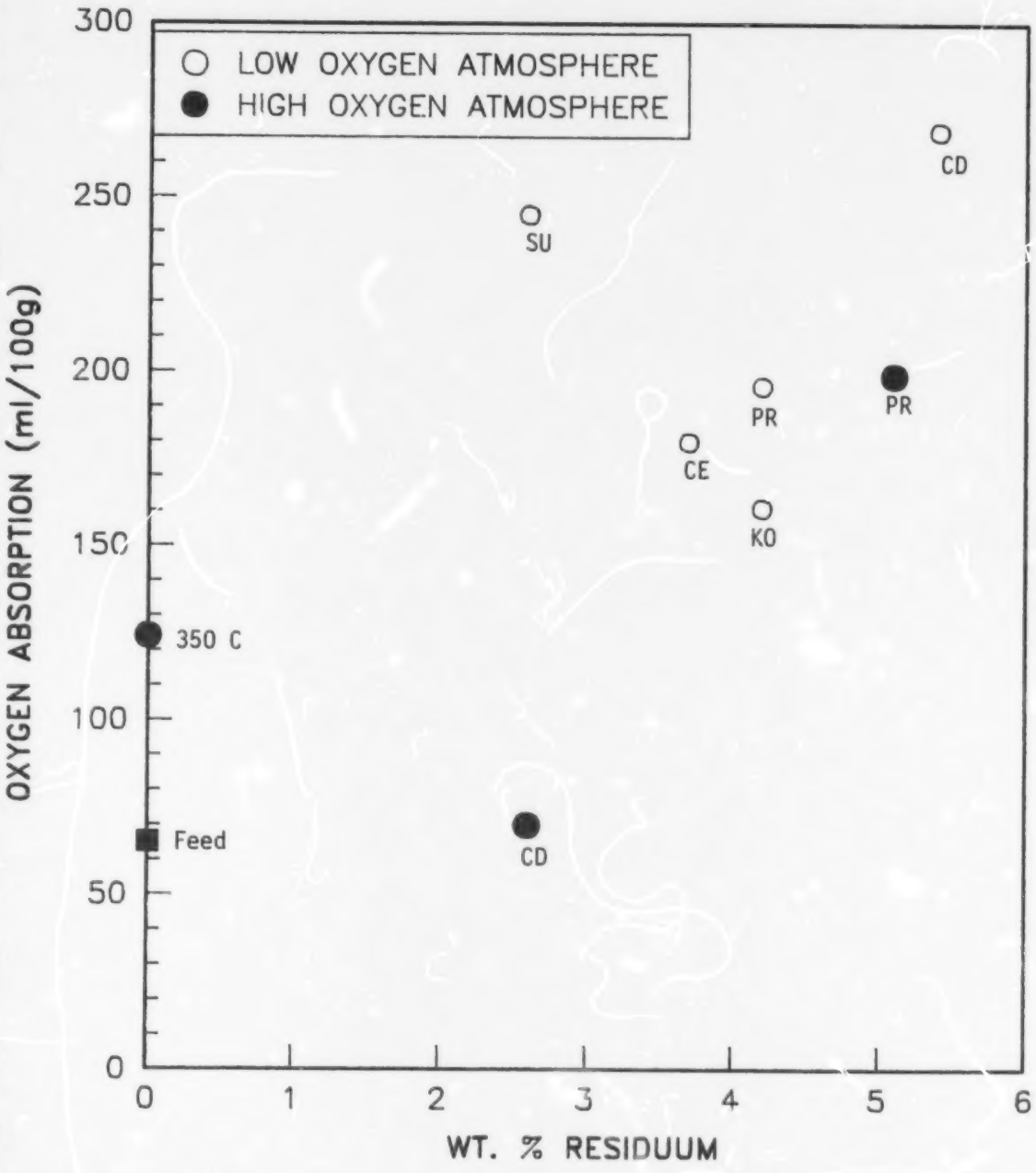


FIGURE 15:

CARBON MONOXIDE PRODUCTION FOR OBED COAL USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

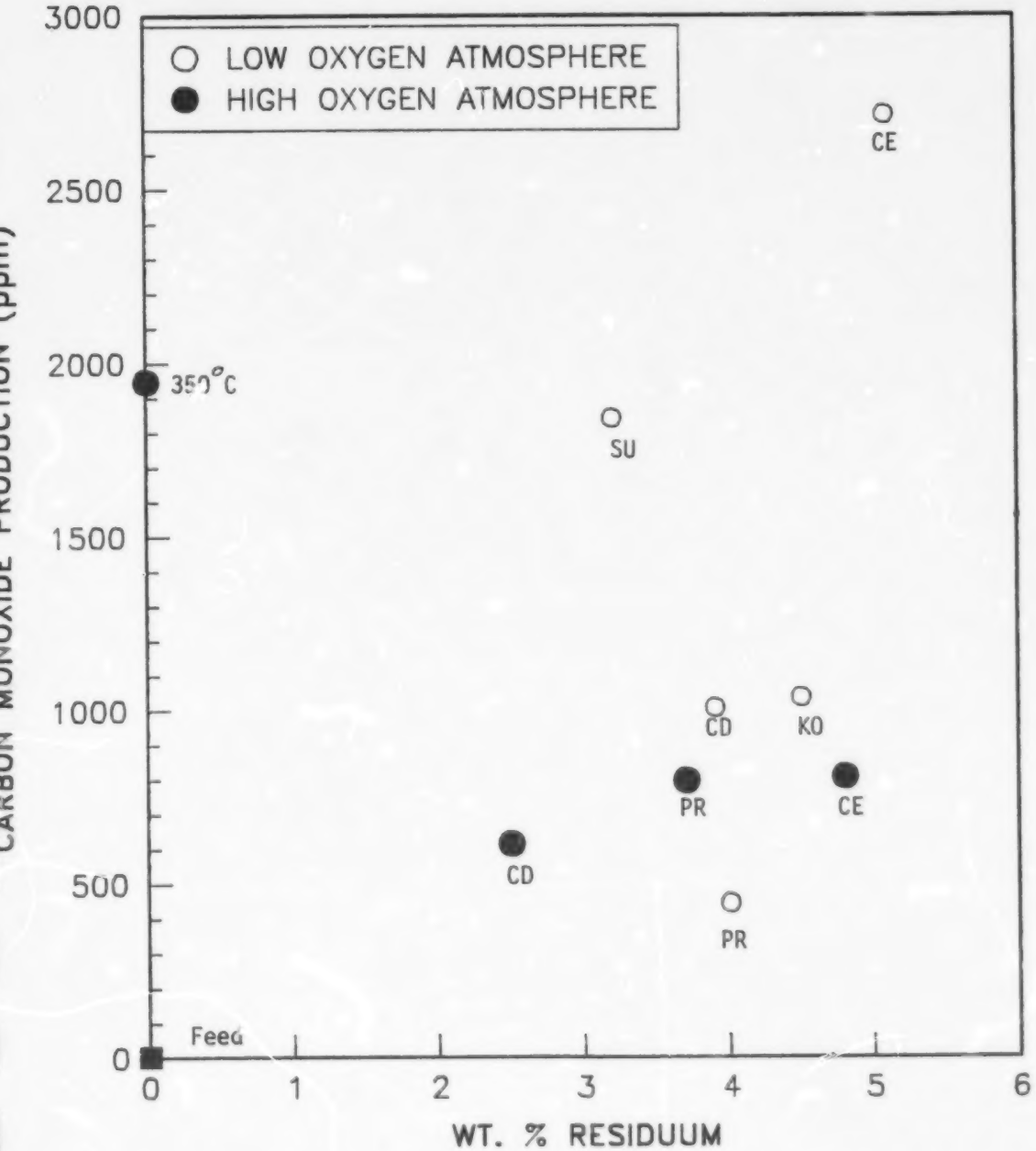


FIGURE 16:

CARBON MONOXIDE PRODUCTION FOR HIGHVALE COAL USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

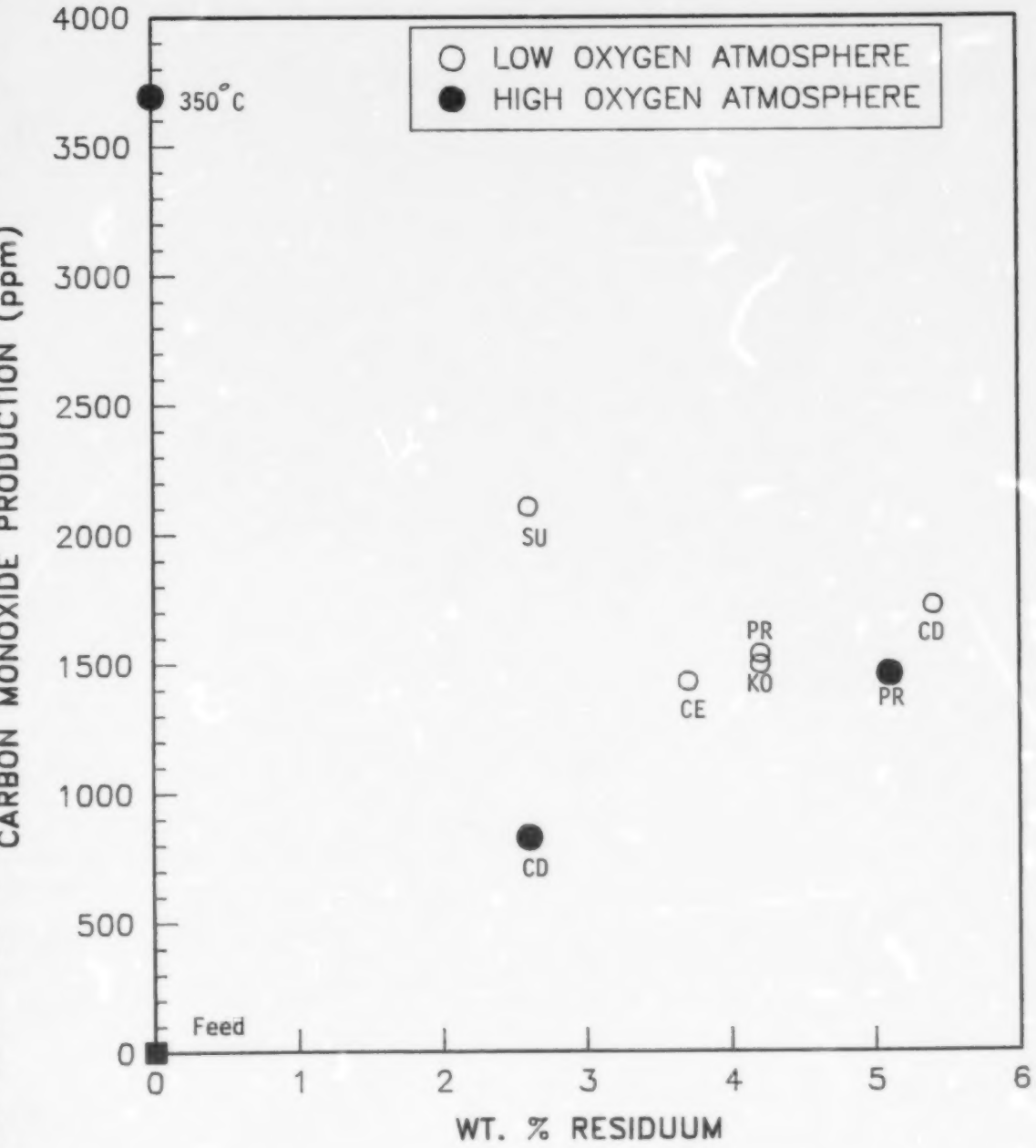


FIGURE 17:

CARBON MONOXIDE PRODUCTION VS. OXYGEN CONSUMPTION FOR OBED COAL USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

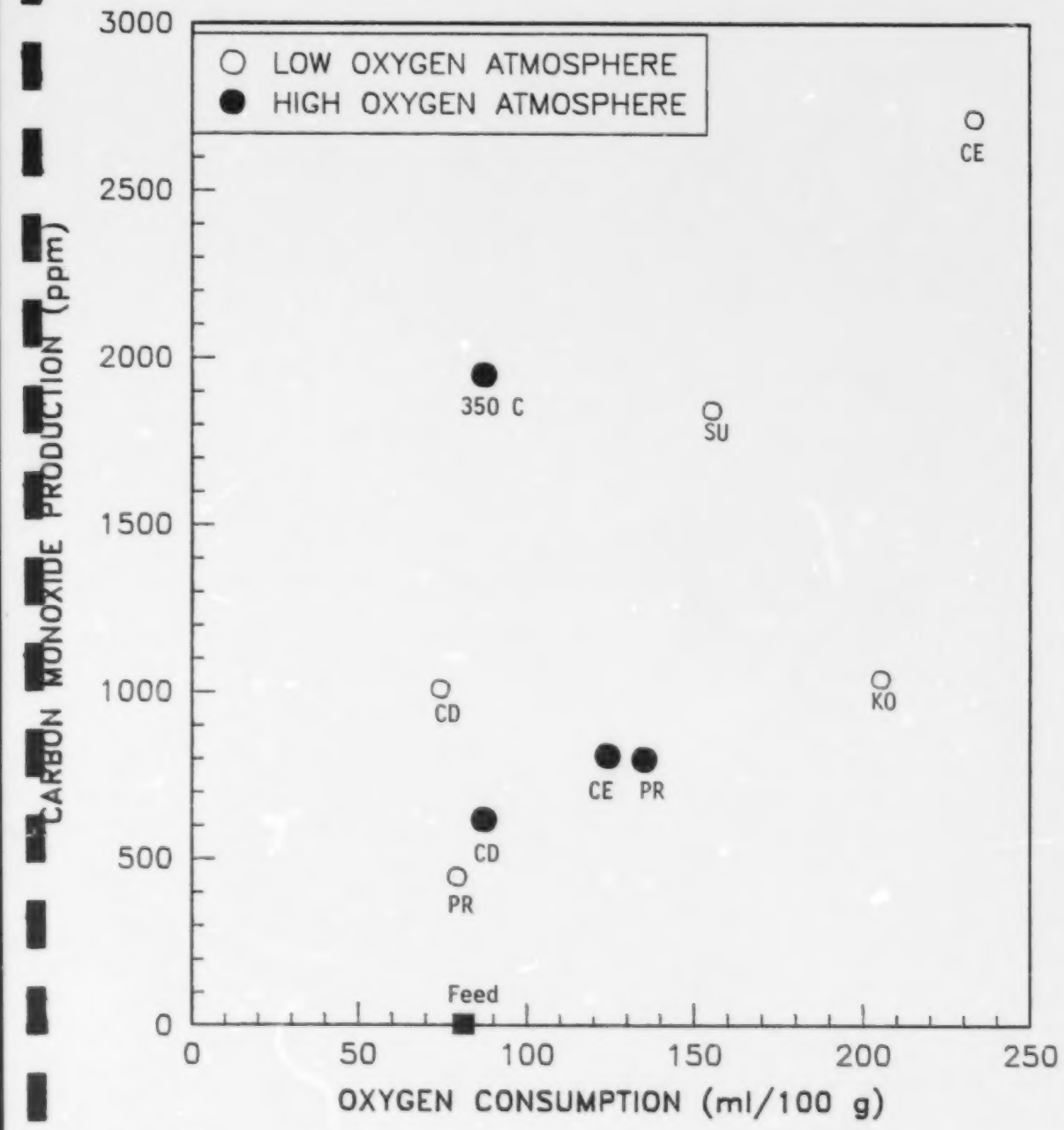


FIGURE 18:

CARBON MONOXIDE PRODUCTION VS. OXYGEN CONSUMPTION
FOR HIGHVALE COAL
USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

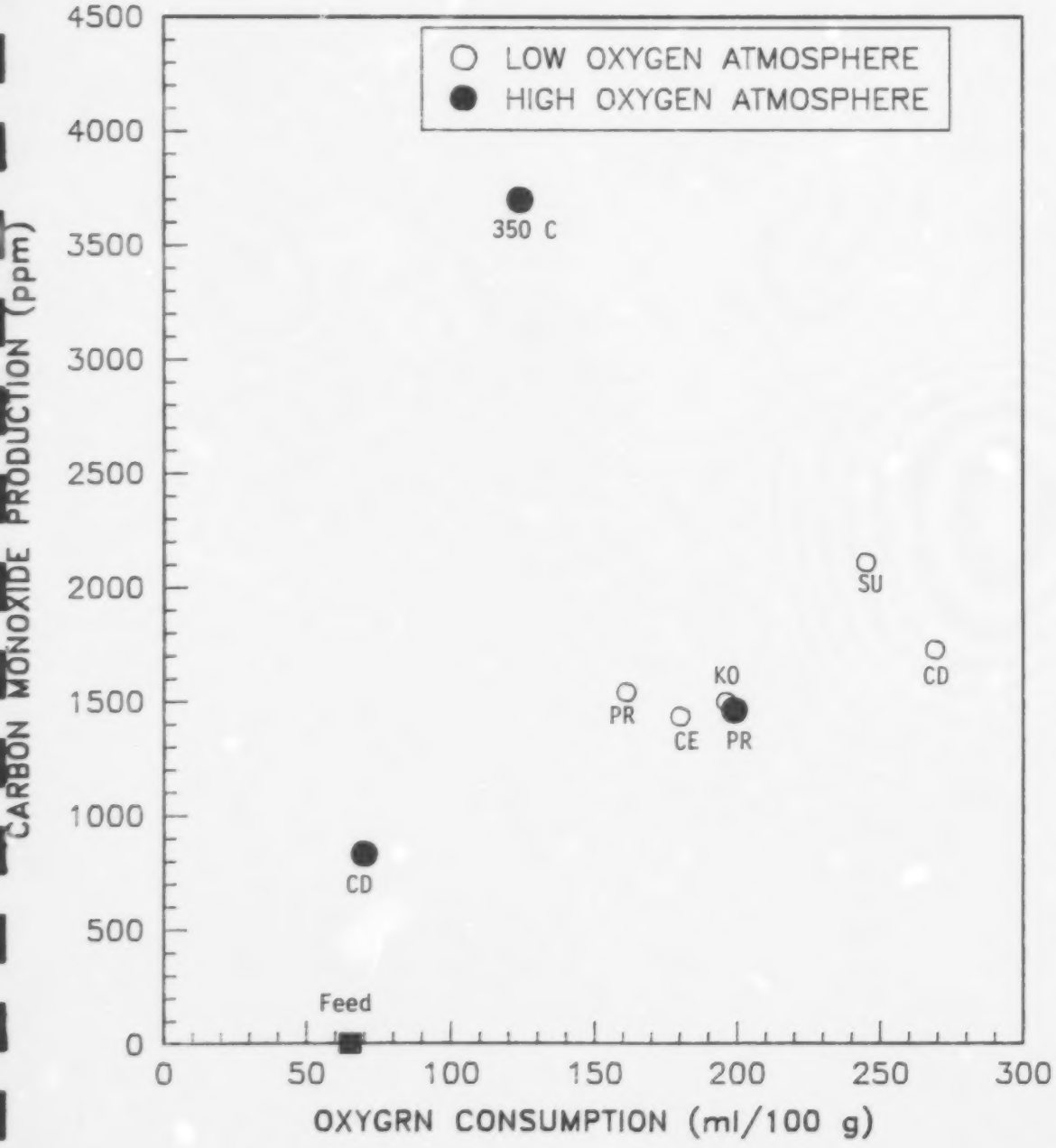


FIGURE 19:

RATIO OF CARBON MONOXIDE PRODUCED TO OXYGEN CONSUMED FOR OBED COAL USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM

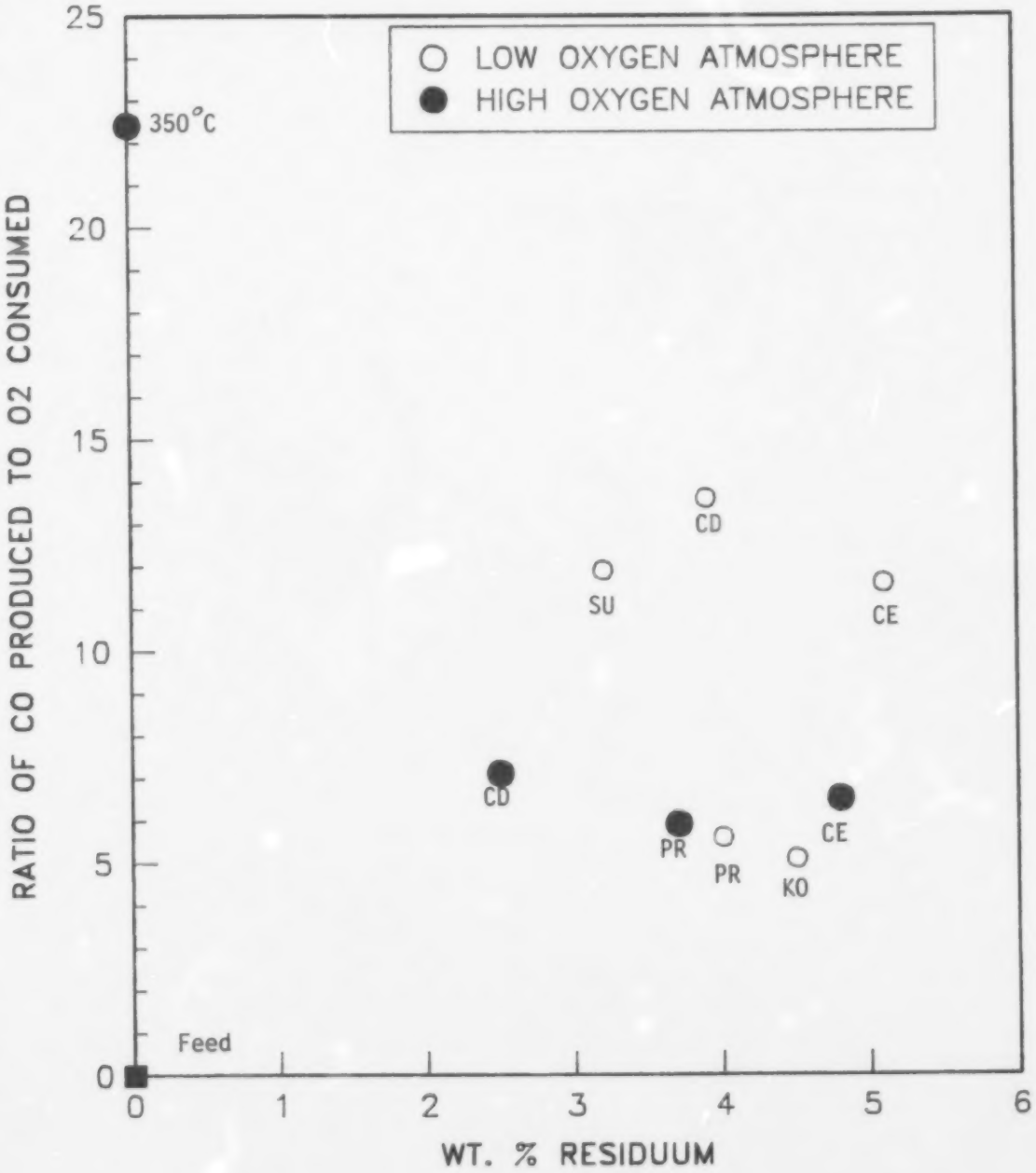
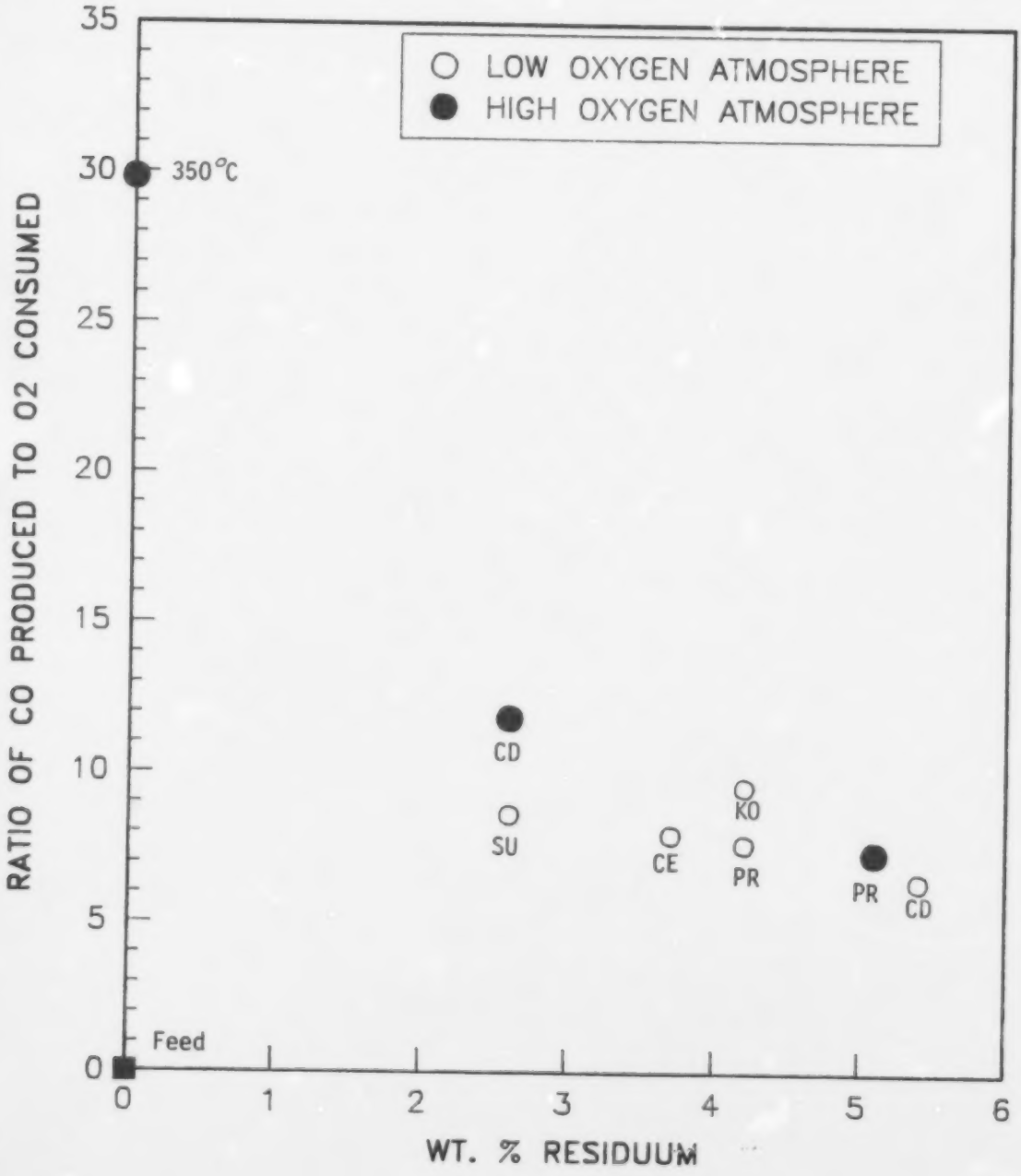


FIGURE 20:
RATIO OF
CARBON MONOXIDE PRODUCED TO OXYGEN CONSUMED
FOR HIGHVALE COAL
USING HIGH AND LOW OXYGEN LEVELS IN TREATING DRUM



Appendix 1

Work Statement of Research Contract
06.SQ.23440-7-9197

TASK NO. 1
COAL SAMPLE ACQUISITION AND CHARACTERIZATION

Two coal samples will be acquired for this research program. Coal samples recommended for this study are Coal Valley (Bituminous C) and Highvale (Subbituminous B) coals. These coals represent major thermal coal reserves in Alberta; and their higher moisture contents make them the preferred feedstocks for studying beneficiation based on moisture reduction.

Approximately 1,000 kg of each sample will be obtained from these mines. Acquisition of samples will be the responsibility of Gulf; but assistance from CANMET may be required in confirming that these samples are utilized for a research project, jointly funded by Gulf and the Dept. of Energy, Mines, and Resources.

The coal samples obtained will be prepared to a top size of 12.7 mm, and screened at 3.2 mm. Only the size fraction 12.7 mm x 3.2 will be used in this study. A representative sample will be extracted and characterized for proximate and ultimate analyses, and equilibrium moisture.

In addition, in order to determine the effect of various residua and their penetration into coal pores, pore volume and pore size distribution will be assessed.

The N_2 Method (BET) will be utilized for this evaluation. Alberta Research Council's coal department at Devon will be the sub-contractor for this evaluation.

TASK NO. 2
RESIDUUM SAMPLE ACQUISITION AND CHARACTERIZATION

Five residuum samples, from various sources and operations, and with large variations in properties, will be obtained and studied in this research program. The quantity required for each residuum is in the order of ten gallons. Acquisition of residuum samples, Again, will be the responsibility of Gulf with assistance from CANMET.

The five residuum samples recommended are:

- Zero pen asphalt
- PDA (asphalt from propane deasphalted vacuum tower bottoms)
- CANMET residuum
- Heavy oil residuum
- Coal tar

These samples cover pitch materials originated from conventional crude, heavy oil, and coal. The operations involved expand from current petroleum refinery, heavy oil upgrading processes, and coke oven operation.

In order to have a complete data base for these residuum samples, both physical and chemical properties will be determined. The proposed analysis, method of analysis, and sub-contractors are detailed in the following table.

PHYSICAL PROPERITES

ANALYSIS	METHOD OF ANALYSIS	SUB-CONTRACTOR
Specific Gravity	Parr Density	ARC - Coal Dept.
Softening Point	ASTM Specification	
Penetration	ASTM Specification	
Viscosity @ 2 Tempts.	ASTM Specification	ARC - Coal Dept.
Molecular Weight	Vapor Pressure Osmometry	ARC - Coal Dept.
Molecular Weight distribution	Gel Permeation	ARC - Coal Dept.

CHEMICAL PROPERTIES

Analysis	Method of Analysis	Sub-Contractor
Simulated Distillation	Crude	ARC - Coal Dept.
Elemental Analysis (C, H, N, S)	ASTM Specifications	ARC - Coal Dept.
Component Type Analysis	Iatroscan Method	ARC - Coal Dept.
Aromatics by Ring Size	Iatroscan Method	ARC - Coal Dept.
Aromaticity	C13NMR	ARC - Coal Dept.

Analyses of physical and chemical properties should provide sufficient background information on these residuum samples. However, it should be pointed out that additional analyses may be required as the project moves along to ensure the accomplishment of the task objective. Additional analyses are not anticipated to constitute a major cost component.

TASK NO. 3

EFFECT OF HEAT TREATMENT ON RESIDUUM PROPERTIES

Gulf's beneficiation method injects residuum onto coal particles heated in a drum dryer. At point of injection, temperatures are typically between 200°C to 300°C. Depending on the types of residuum used, light ends may be evaporated and the properties of the "real" residuum that gives coal beneficiation may be quite different from those of virgin materials. The characterization of the properties of the "real" residuum that participates in the coal beneficiation process is of fundamental importance.

The effect of heat treatment on residuum properties can be determined with high degree of confidence using thermogravimetric analysis (TGA). The following conditions of TGA experiments are proposed:

- Temperature range : ambient to 300°C
- Rate of temperature programming : 20°C/min
- Gas atmosphere : 10% oxygen
- Residue at 300°C will be collected and characterized for chemical properties as tabulated in Task No. 2.

Both the TGA experiments and characterization of chemical properties will be sub-contracted to ARC's Coal Department in Devon.

The physical properties of the "real" residuum samples, however, cannot be determined from the small amounts of residue left over after the TGA experiments. To provide larger quantities of residue for physical properties determination, a special furnace will be designed and constructed. The furnace will simulate the operating conditions used for the TGA experiments (temperature programming, gas atmosphere, etc.), and will be mounted on a balance to monitor weight loss as a function of temperature. Off gas will be sampled and analyzed by gas chromatography.

About 10 - 20 gm of residuum samples will be used in this "macro-scale thermogravimetric" furnace designed and built for this task. The residuum left over at 300°C will be subjected to physical properties determinations as outlined in Task No. 2. Weight loss curves of residuum samples from this furnace will be compared with the results of TGA study.

TASK NO. 4

BENEFICIATION EXPERIMENTS AT CONTROLLED CONDITIONS

To correlate the degree of coal beneficiation with the properties of residuum, coal beneficiation experiments at controlled conditions will be carried out. Two series of experiments are planned and each series will use one single coal sample. In each series, two levels of temperatures will be used to include any temperature effects on the level of upgrading. The conditions for these beneficiation experiments for each series using the pilot scale drum dryer are as follows:

- Temperature level: 200°C and 300°C
- Coal feed rate: 20 kg/hr
- Residuum feed rate: 4% of coal feed rate.

A total of 20 experiments will be carried out in this task. (2 coal samples x 2 temperature levels x 5 residuum types = 20 runs.)

The upgraded products will be characterized for the following qualities to evaluate the degree of upgrading:

- Residual moisture content - level of drying
- Equilibrium moisture - level and penetration into coal pores
- Residuum content - level of residuum coating.

The difference in residuum input set at the displacement pump and residuum determined on the product will be compared with the thermogravimetric data obtained in Task No. 3. Residuum content will be checked by mixing known amounts of residuum and coal to confirm if there is any irrevisible bonding between coal and residuum.

In addition to these analyses, approximately 6 - 8 products will be selected and evaluated for pore volume and pore size distribution. These data will be useful to correlate the degree of penetration with molecular size and compositional breakdown of residuum samples.

TASK NO. 5

RESIDUUM PROPERTIES AFTER COAL BENEFICIATION

In addition to the determinations of beneficiation levels obtained in Task No. 4, a 500 gm split of each product will be subjected to extraction to recover the residuum. The level of residuum determined in this task will be compared with those obtained in Task No. 4.

Ten selected residuum samples recovered in this task will be characterized as in Task No. 2. The changes of properties will be compared and correlated with those obtained in thermogravimetric evaluation (Task No. 3).

The characterization of residuum will be subcontracted to Alberta Research Council, Coal Department.

TASK NO. 6
RESULT ASSESSMENT AND FINAL REPORT PREPARATION

The results on residuum properties determined in Task 2, 3, and 5 will be critically compared to investigate the effect of heat treatment on residuum qualities and characteristics.

All these data will be correlated with the degree of coal beneficiation as obtained in Task No. 4. These correlations will form the basis for future choice of residuum and give a good understanding for process development.

A final report containing all data, interpretation of data, supported by tables and graphs will be prepared for submission.

Appendix 2

Thermogravimetric Analysis (TGA)
Thermograms of Five Residua

FIGURE 1A

34-88

TGA

Sample: SF-881421 CENEX PDA
Size: 5.36 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0

Date: 8-Sep-88 Time: 12:54:16
File: SQ.04 42
Operator: AI PT MESH
Plotted: 29-Sep-88 15:50:48

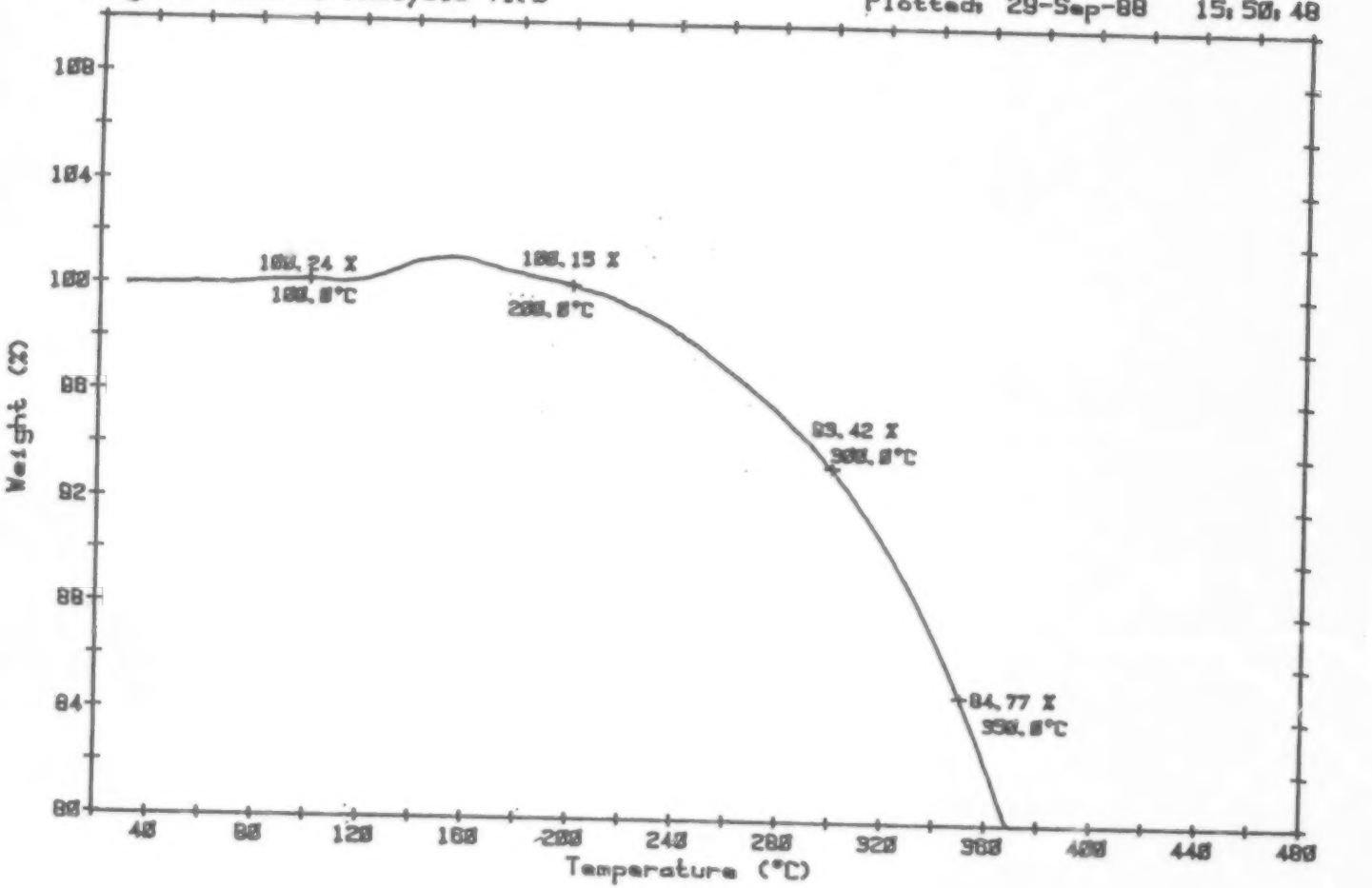


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FIGURE 1B

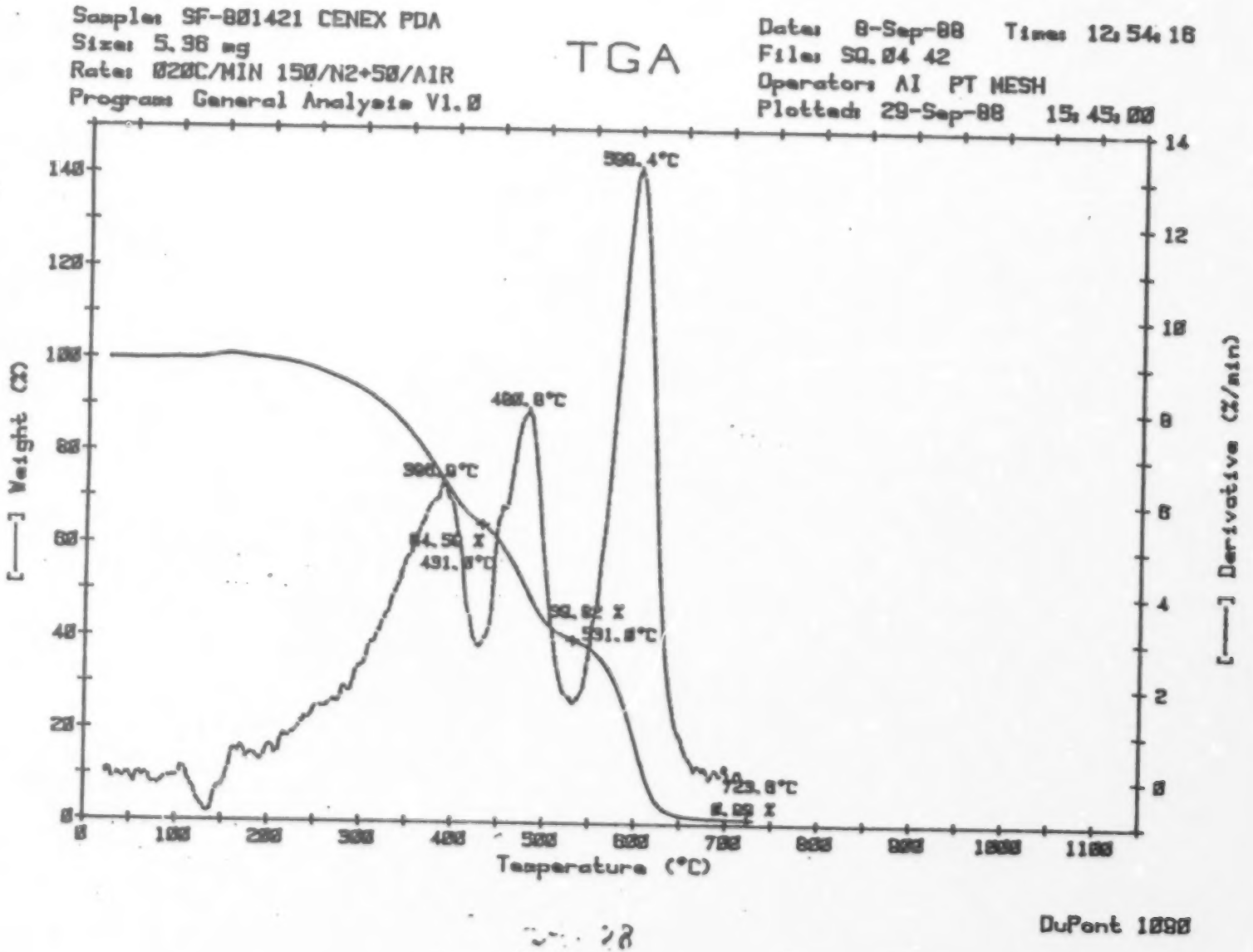
Sample: SF-881421 CENEX PDA
Size: 5.96 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0
TGA
Date: 8-Sep-88 Time: 12:54:16
File: SQ.04 42
Operator: AI PT MESH
Plotted: 29-Sep-88 15:45:00
500.4°C
488.8°C
500.0°C
84.50 %
491.8°C
50.82 %
591.8°C
723.8°C
6.99 %
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
DuPont 1090

FIGURE 2A

33-88

Sample: SF-801421 CENEX PDA
Size: 3.11 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0

TGA

Date: 7-Sep-88 Time: 9:43:12
File: SP.95 42
Operator: AI PT MESH
Plotted: 29-Sep-88 13:26:10

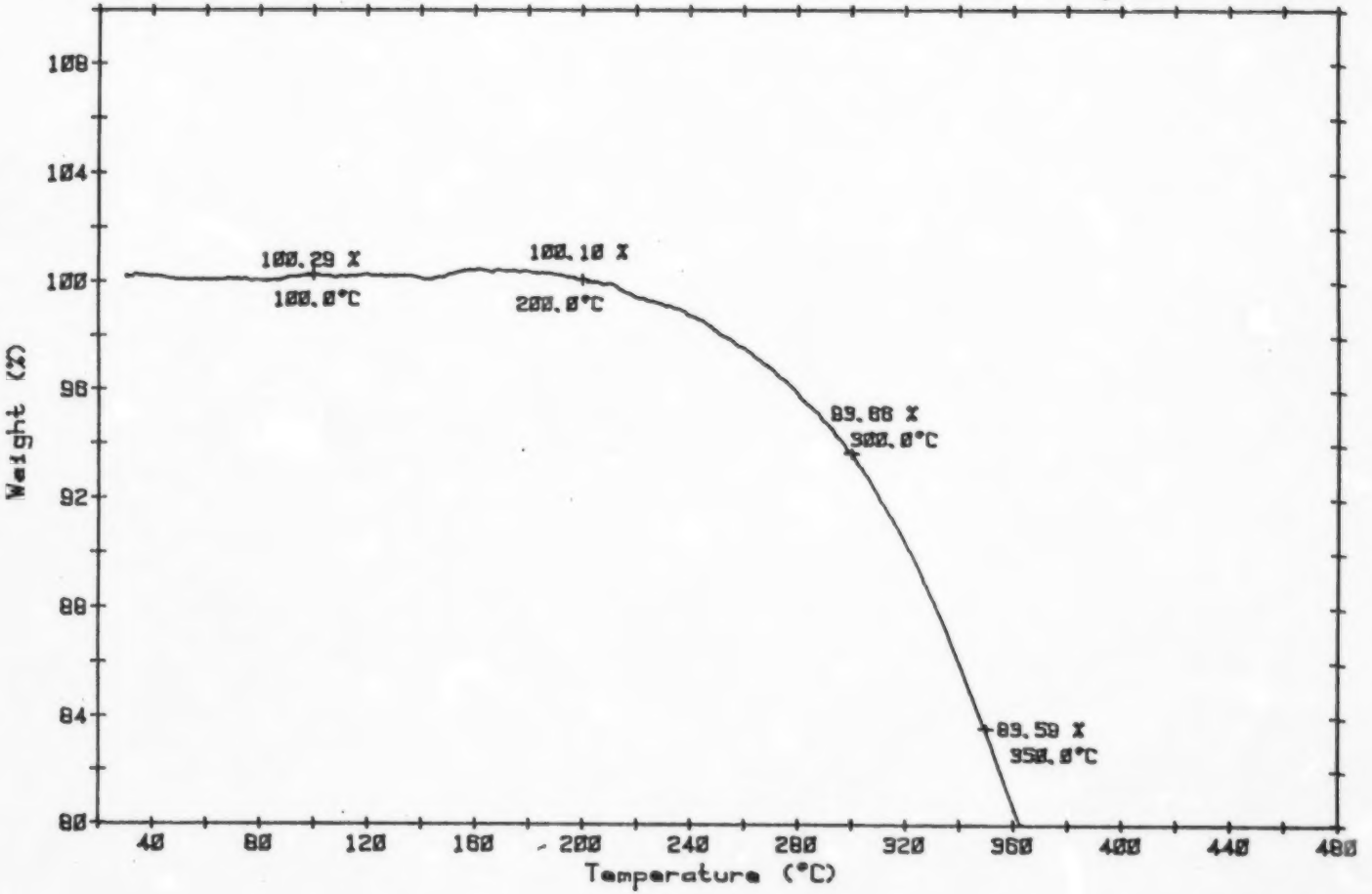

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FIGURE 2B

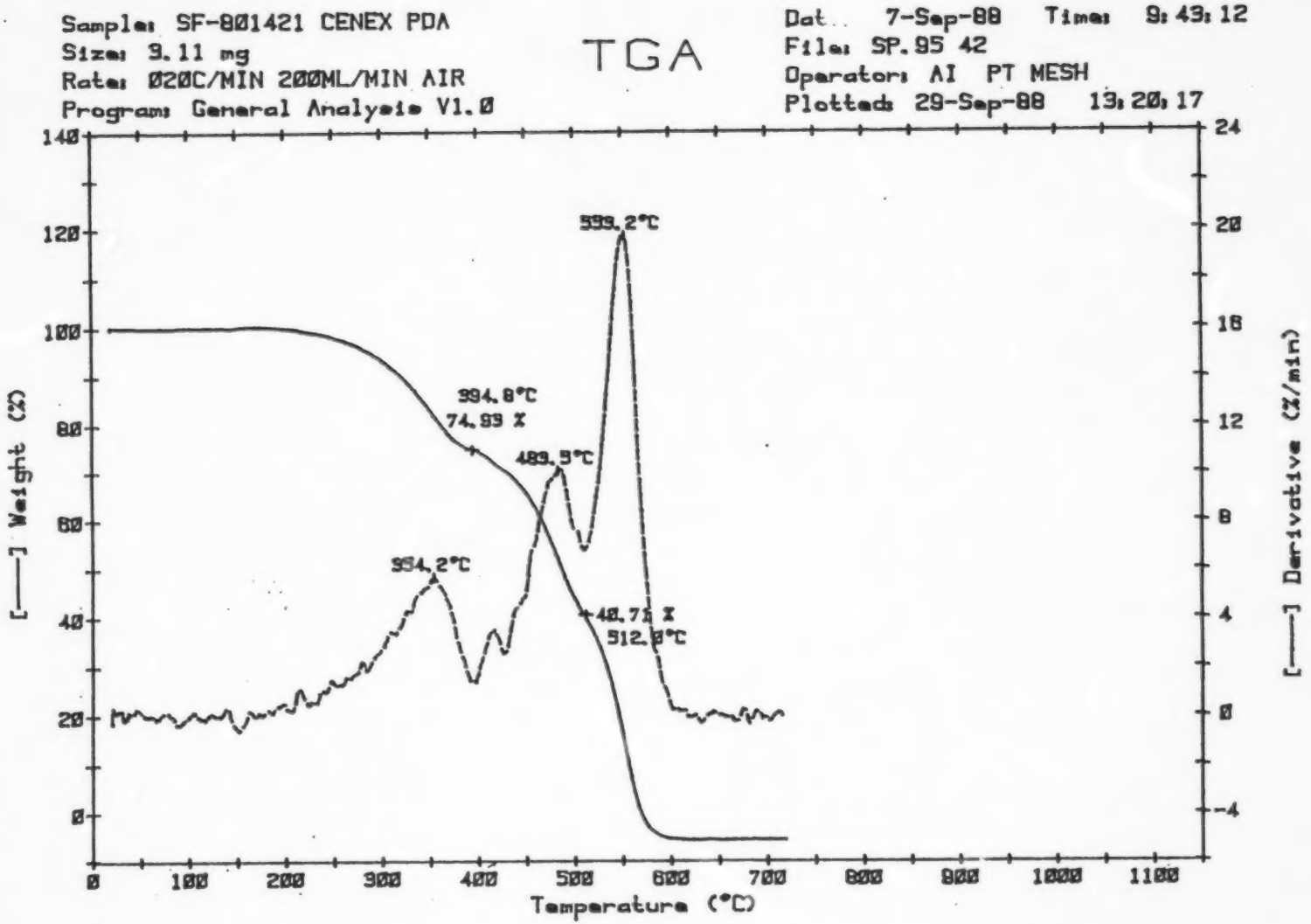

Sample: SF-801421 CENEX PDA
Size: 9.11 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0
TGA
Dat.. 7-Sep-88 Time: 9:43:12
File: SP.95 42
Operator: AI PT MESH
Plotted: 29-Sep-88 13:20:17
599.2°C
494.8°C
74.99 %
489.5°C
954.2°C
40.71 %
512.8°C
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
DuPont 1090

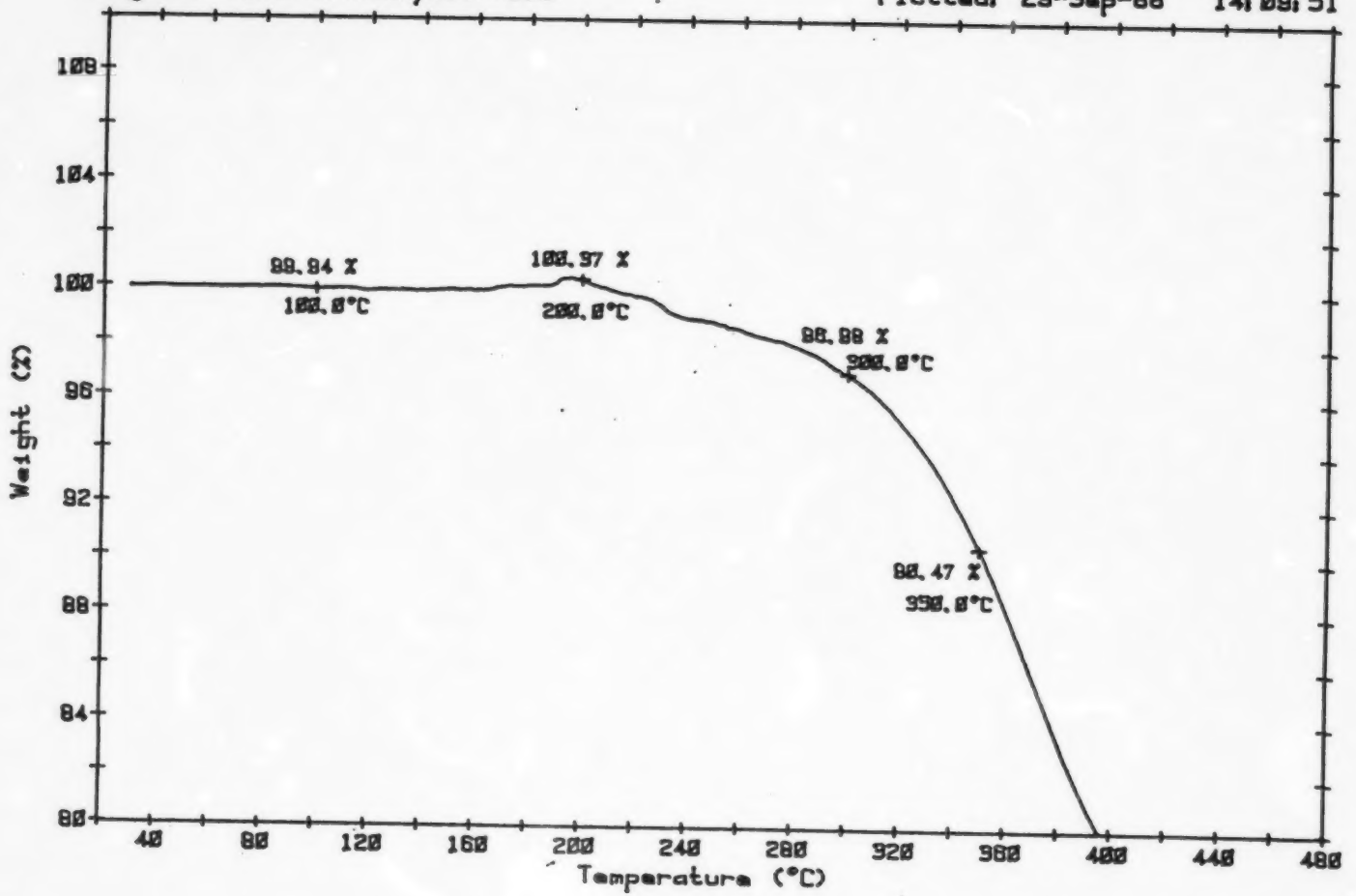
FIGURE 3A

42-88

TGA

Sample: SF-801425 CANMET DEMO
Size: 5.16 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0

Date: 13-Sep-88 Time: 8:58:03
File: SQ.08 42
Operator: AI PT MESH
Plotted: 29-Sep-88 14:09:51



DuPont 1090

FIGURE 3B

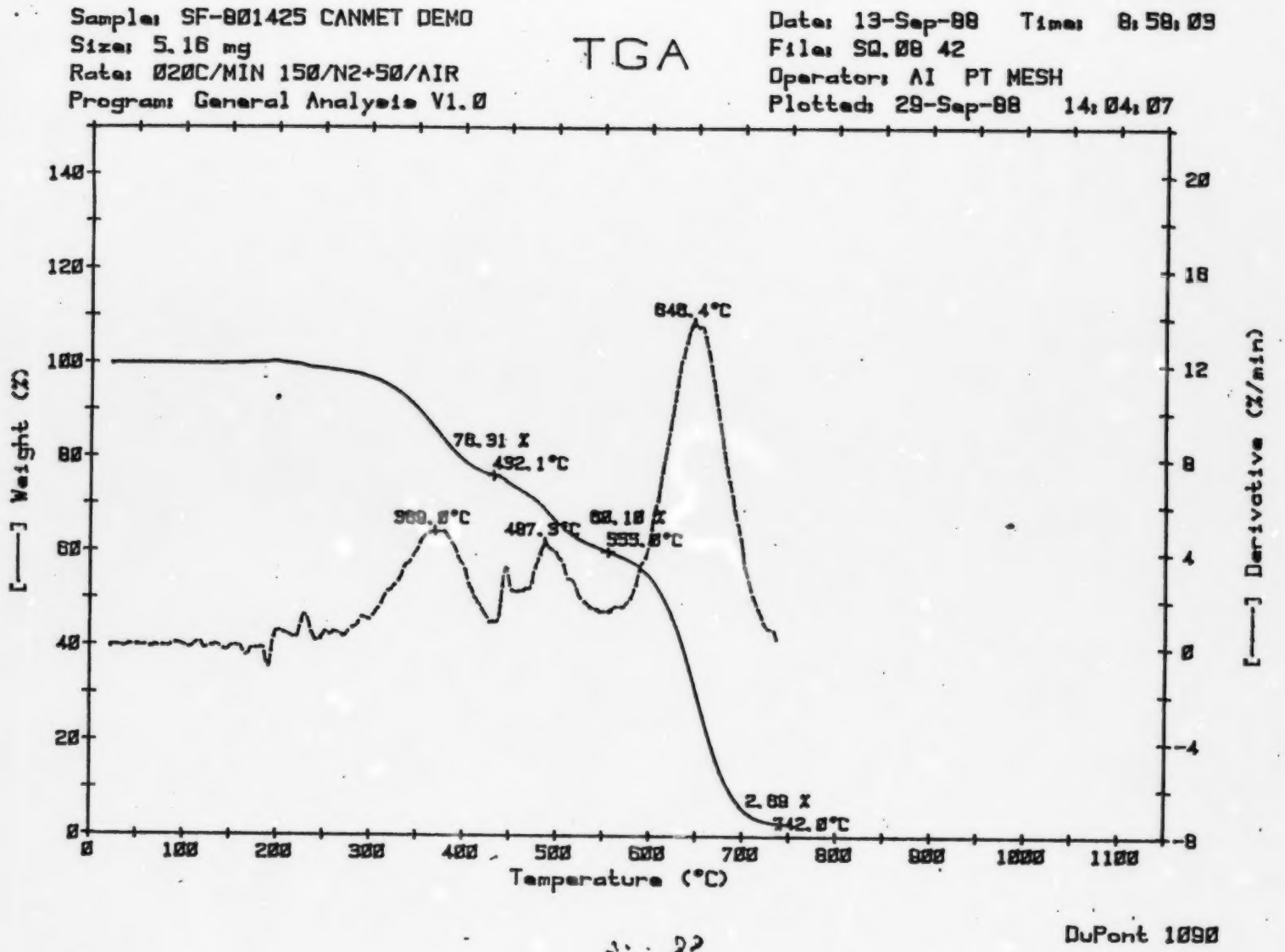

Sample: SF-801425 CANMET DEMO
Size: 5.16 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0
TGA
Date: 13-Sep-88 Time: 8:58:09
File: SQ.08 42
Operator: AI PT MESH
Plotted: 29-Sep-88 14:04:07
78.31 %
432.1°C
969.8°C
487.3°C
88.18 %
555.8°C
848.4°C
2.89 %
742.8°C
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
DuPont 1090

FIGURE 4A

41-98

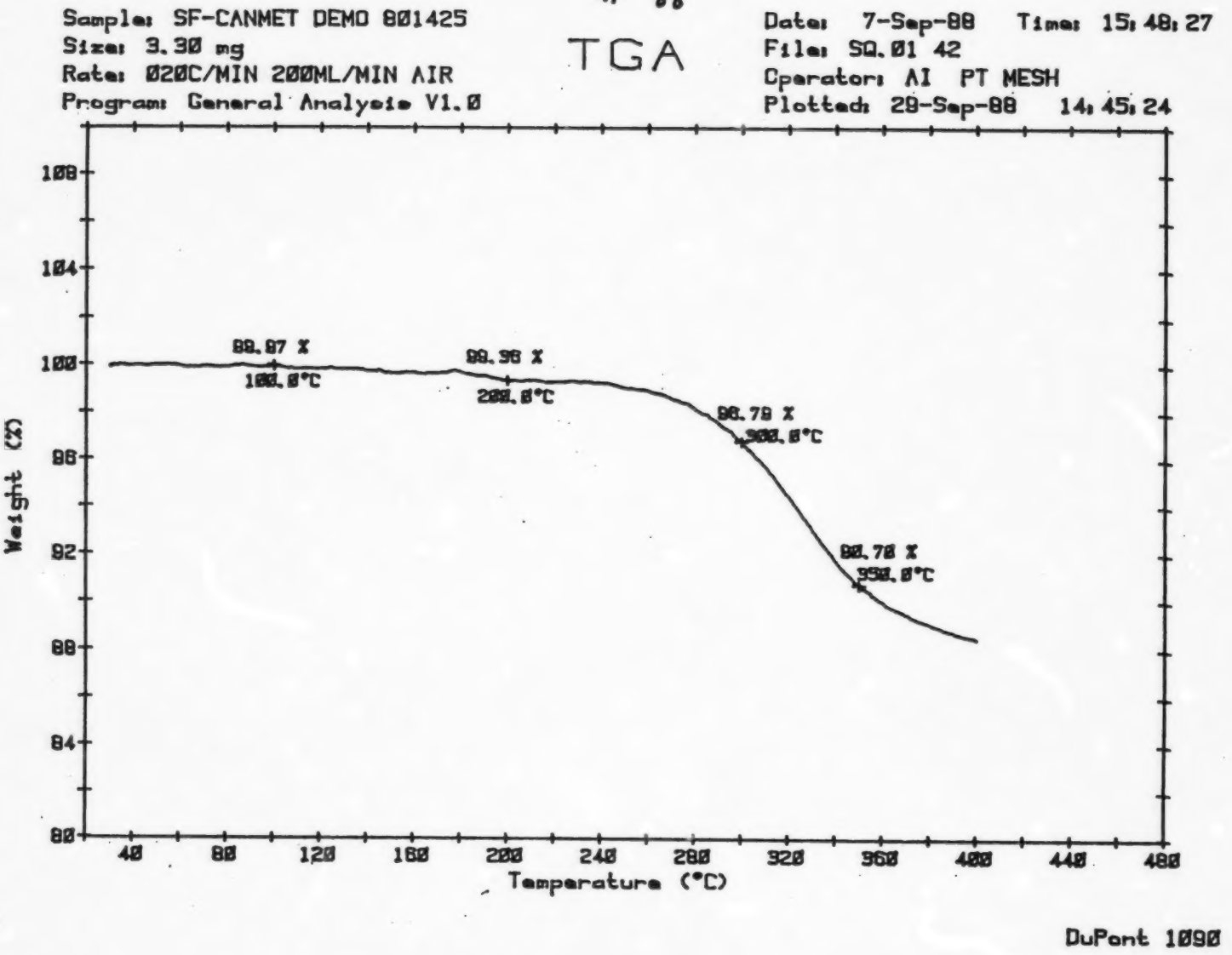


FIGURE 4B

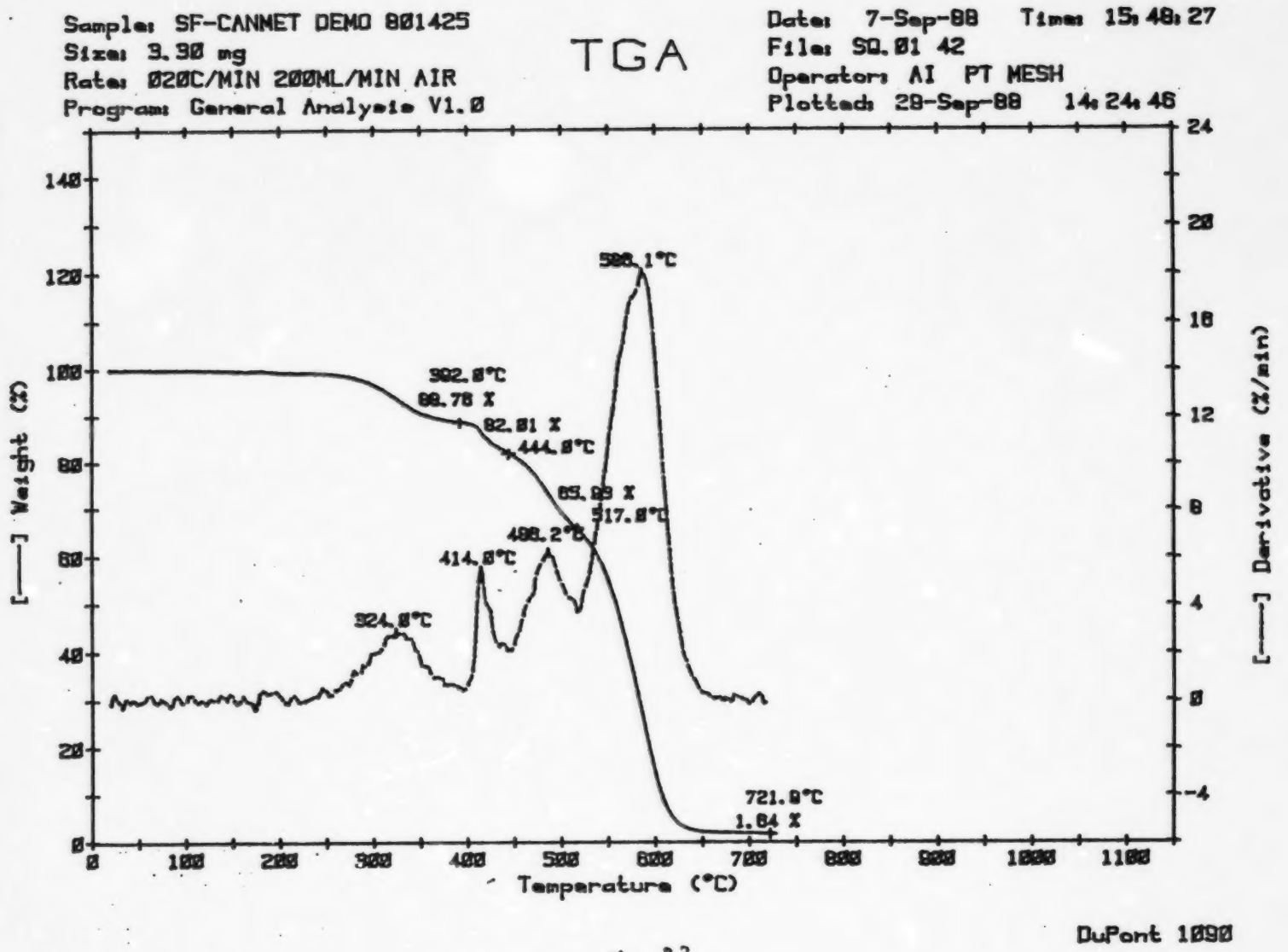

Sample: SF-CANMET DEMO 801425
Size: 3.30 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0
TGA
Date: 7-Sep-88 Time: 15:48:27
File: SQ.01 42
Operator: AI PT MESH
Plotted: 28-Sep-88 14:24:46
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
302.8°C
99.76 %
82.81 %
444.8°C
85.93 %
517.8°C
498.2°C
414.8°C
324.8°C
721.9°C
1.64 %
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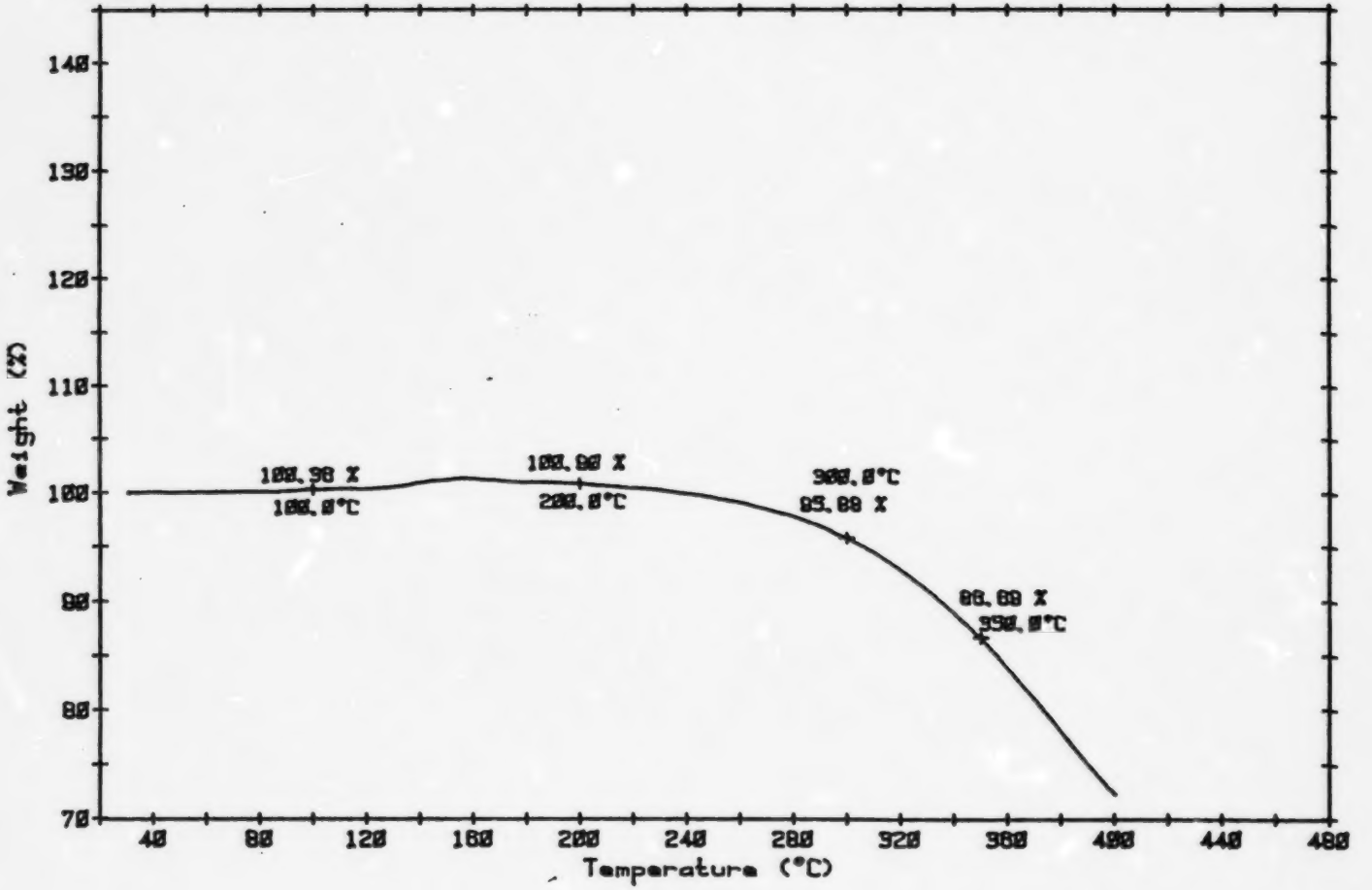
FIGURE 9

40-88

TGA

Sample: SF-881424 PIECE RIVER
Size: 5.00 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0

Date: 8-Sep-88 Time: 19:59:58
File: SQ.05 42
Operator: AI PT MESH
Plotted: 29-Sep-88 15:95:59



DuPont 1090

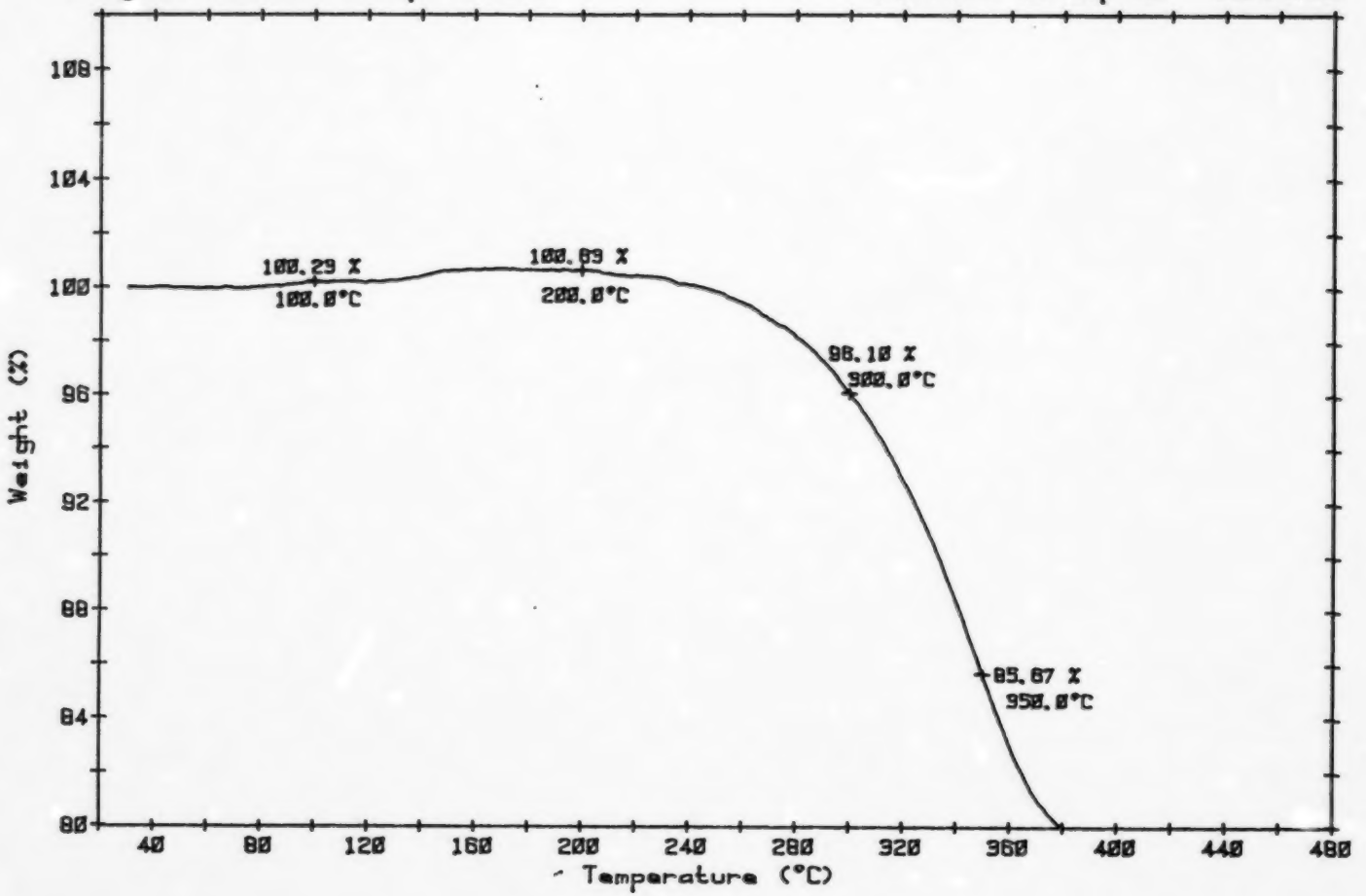
FIGURE 10

39-88

TGA

Sample: SF-801424 PIECE RIVER
Size: 3.98 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0

Date: 7-Sep-88 Time: 10:49:19
File: SP.96 42
Operator: AI PT MESH
Plotted: 29-Sep-88 13:14:02



DuPont 1090

FIGURE 11

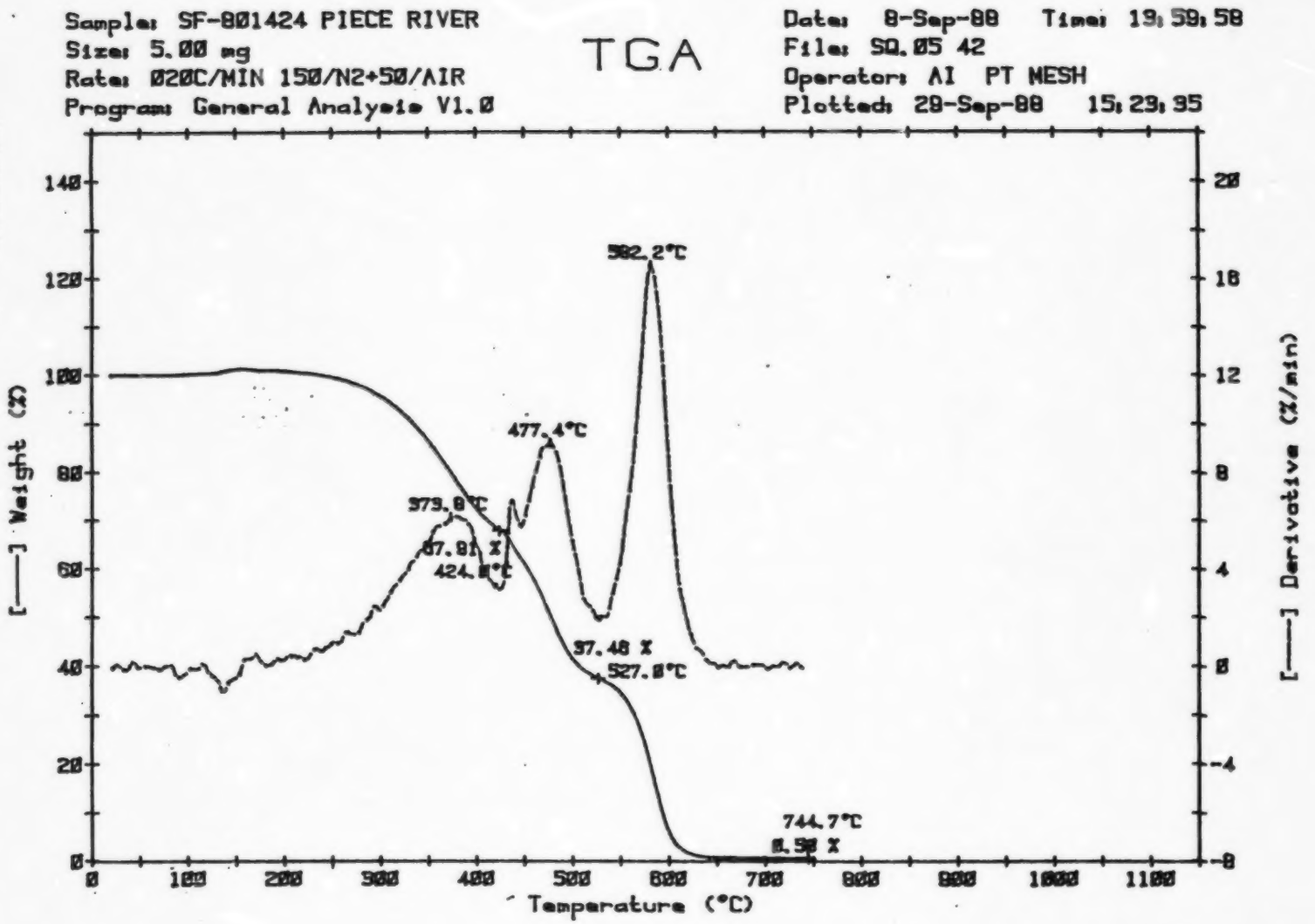


Fig. 22

FIGURE 12

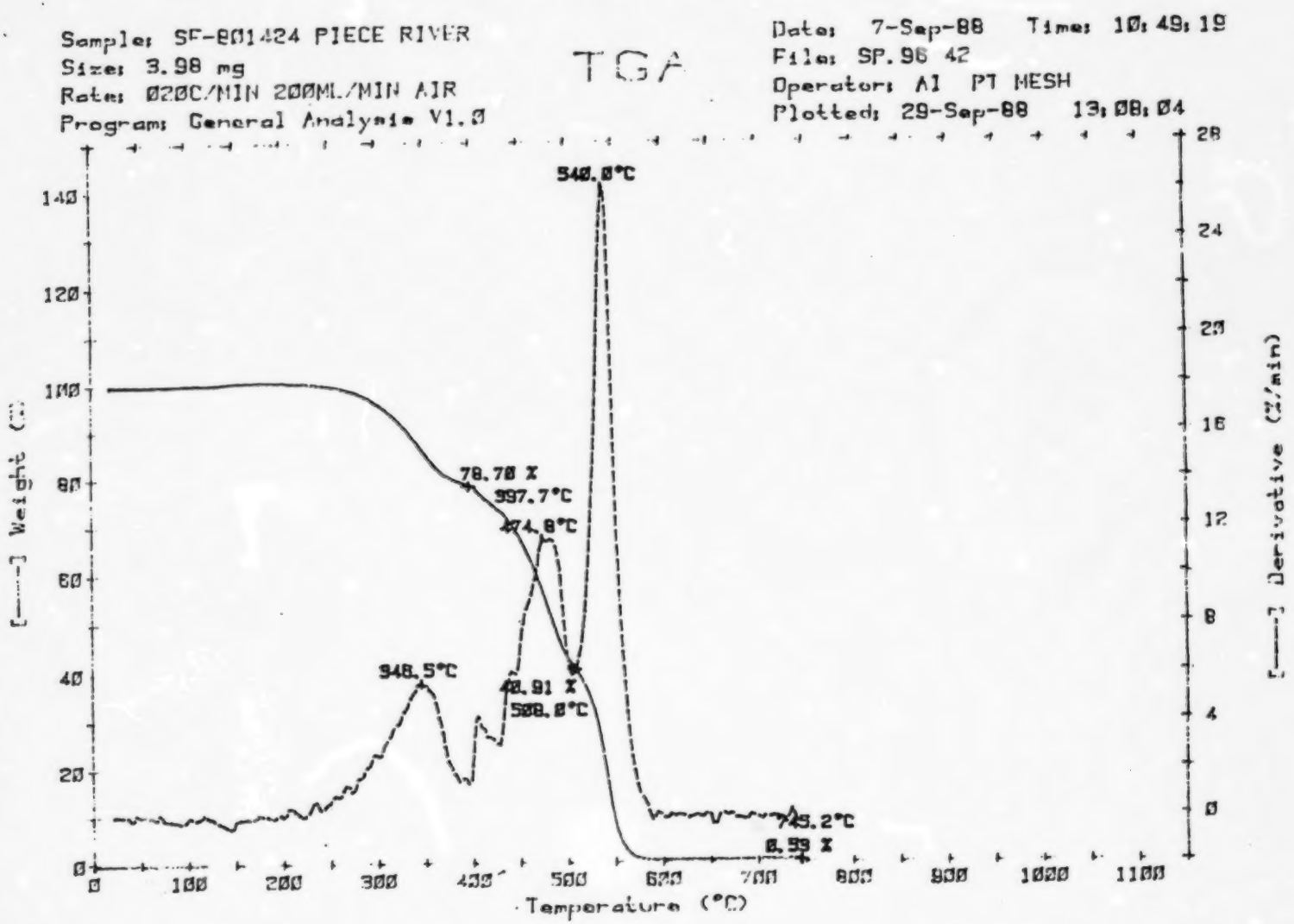

Sample: SF-801424 PIECE RIVER
Size: 3.98 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0
TGA
Date: 7-Sep-88 Time: 10:49:19
File: SP.96 42
Operator: AI PT MESH
Plotted: 29-Sep-88 13:08:04
540.0°C
78.78 %
397.7°C
474.8°C
348.5°C
42.91 %
508.8°C
745.2°C
8.59 %
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
0
100
200
300
400
500
600
700
800
900
1000
1100
140
120
100
80
60
40
20
28
24
20
16
12
8
4
DuPont 1090

FIGURE 13

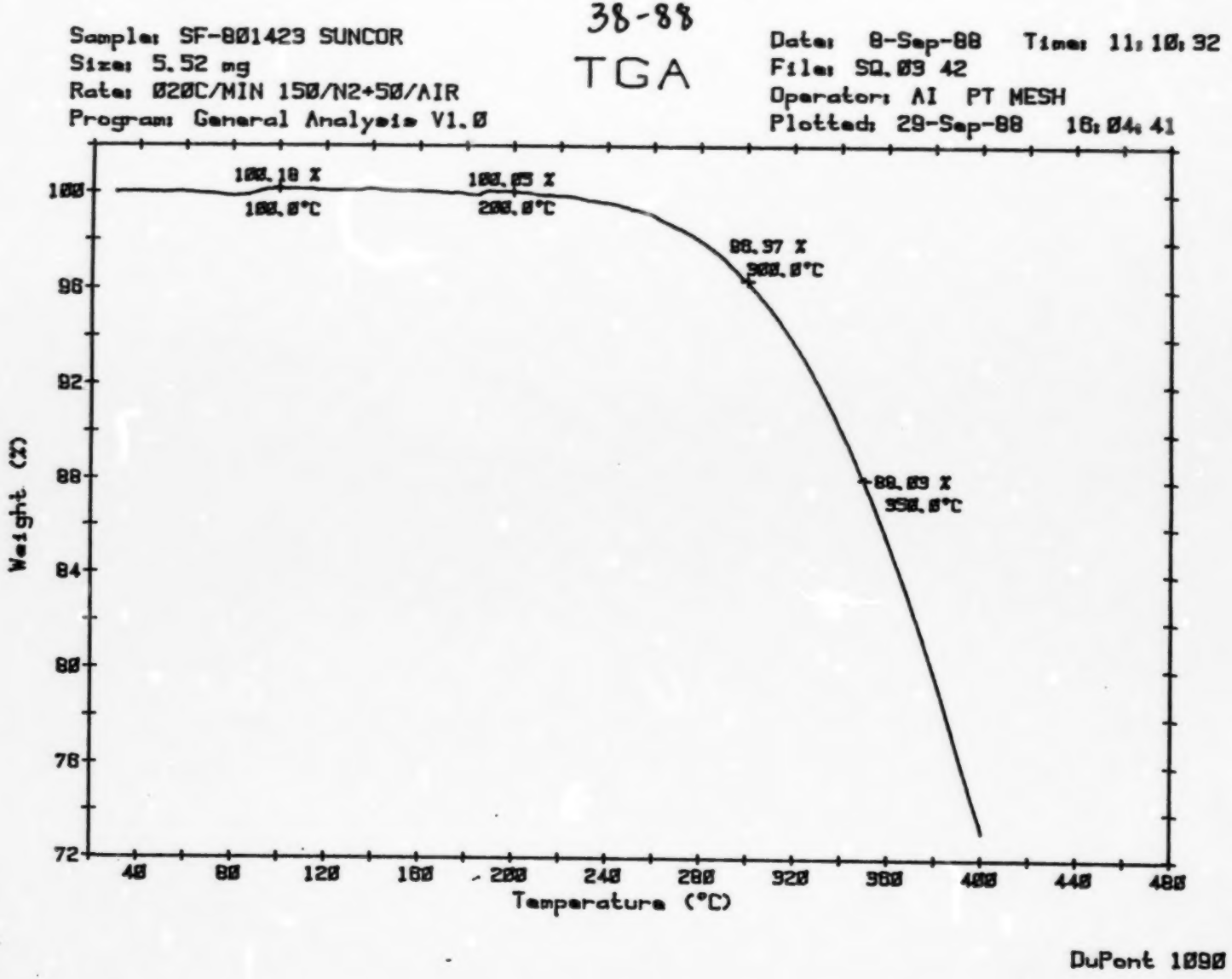

38-88
TGA
Sample: SF-881423 SUNCOR
Size: 5.52 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0
Date: 8-Sep-88 Time: 11:10:32
File: SQ.09 42
Operator: AI PT MESH
Plotted: 29-Sep-88 16:04:41
100.18 %
100.0°C
100.05 %
200.0°C
98.97 %
300.0°C
89.09 %
350.0°C
Weight (%)
100
96
92
88
84
80
76
72
40
80
120
160
200
240
280
320
360
400
440
480
Temperature (°C)
DuPont 1090

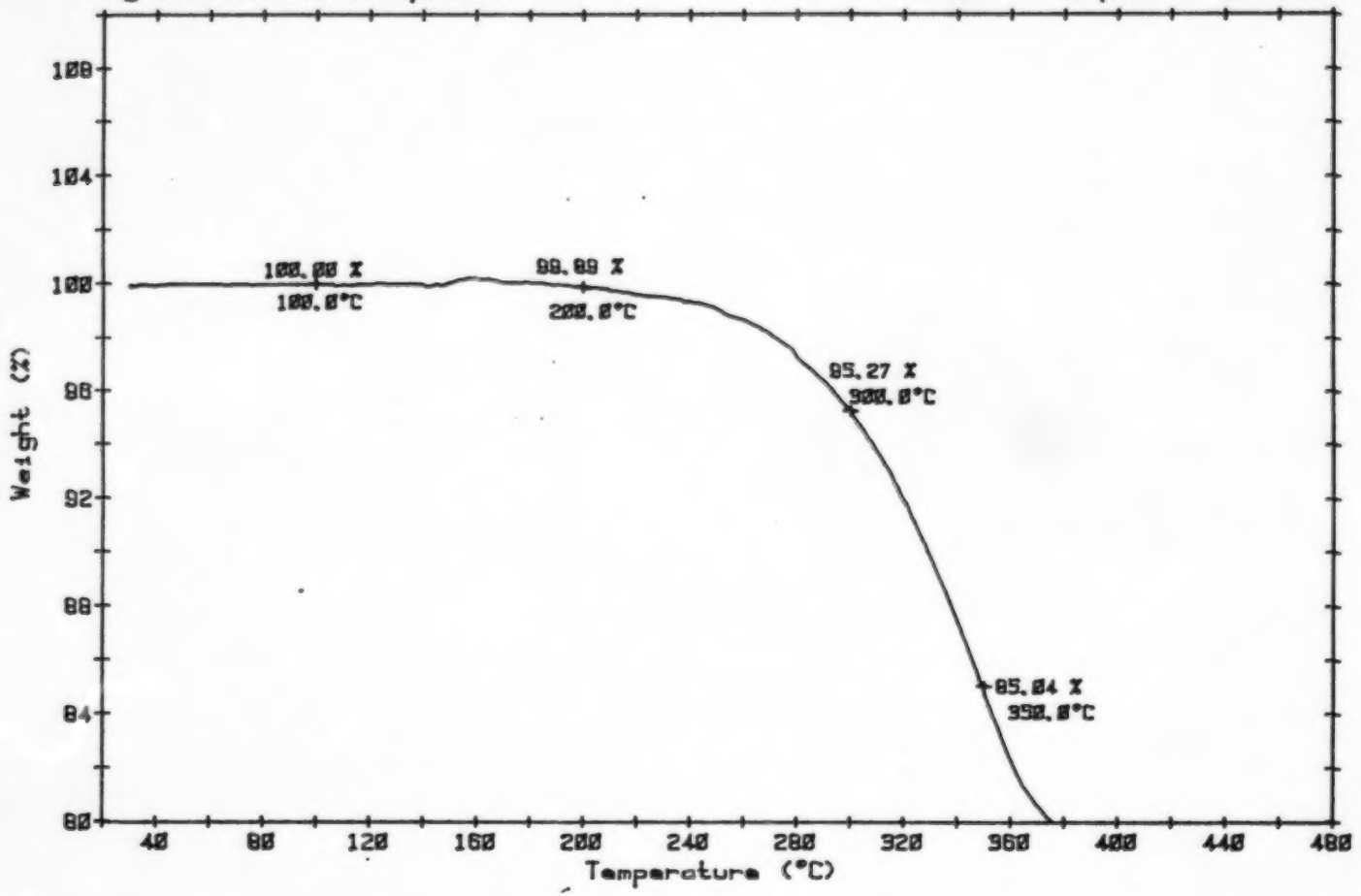
FIGURE 14

37-88

TGA

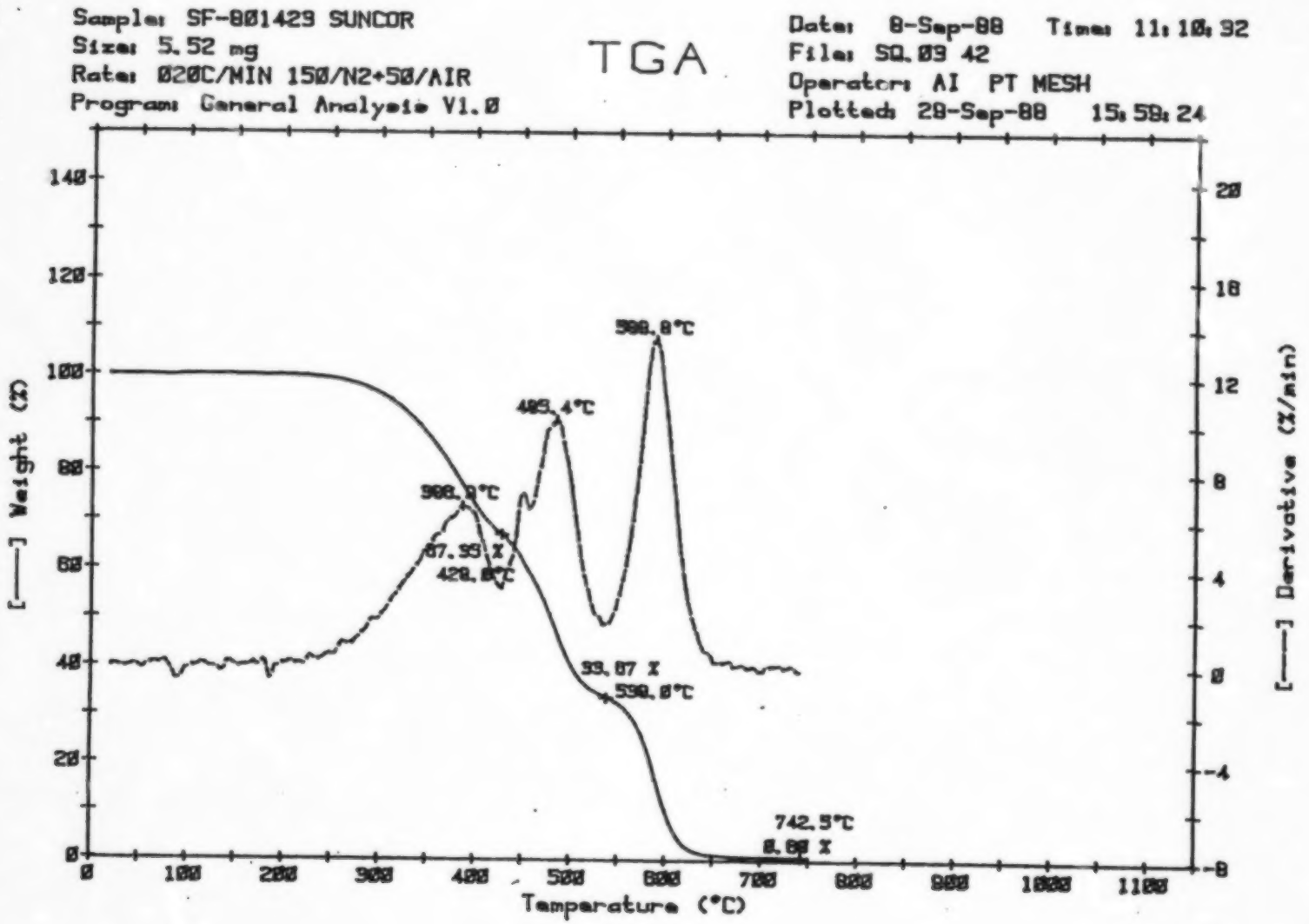
Sample: SF-881423 SUNCOR
Size: 9.55 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0

Date: 2-Sep-88 Time: 13:20:28
File: SP.92 42
Operator: AI PT MESH
Plotted: 29-Sep-88 13:41:12



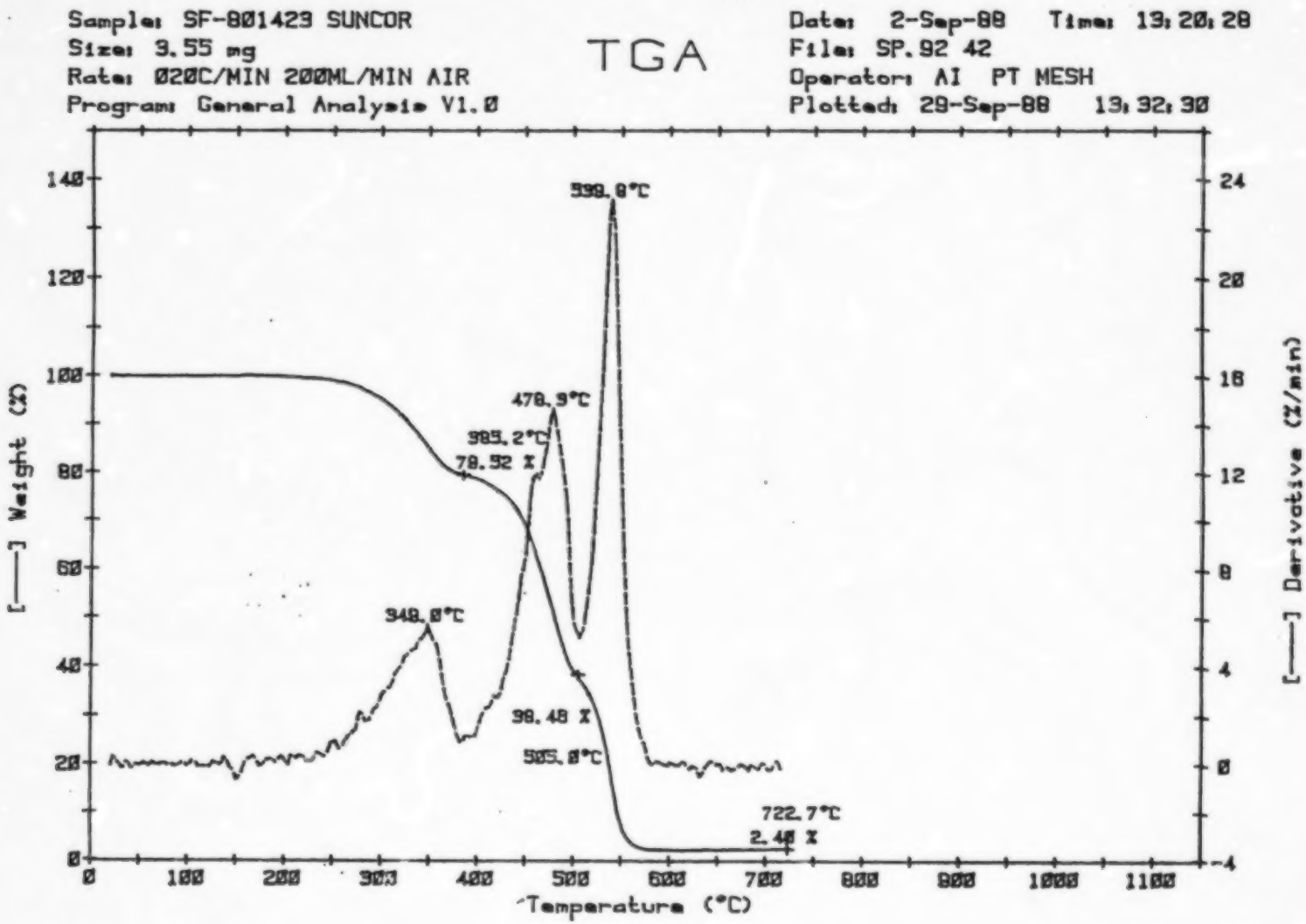
DuPont 1090

FIGURE 15



22.22

FIGURE 16



21-82

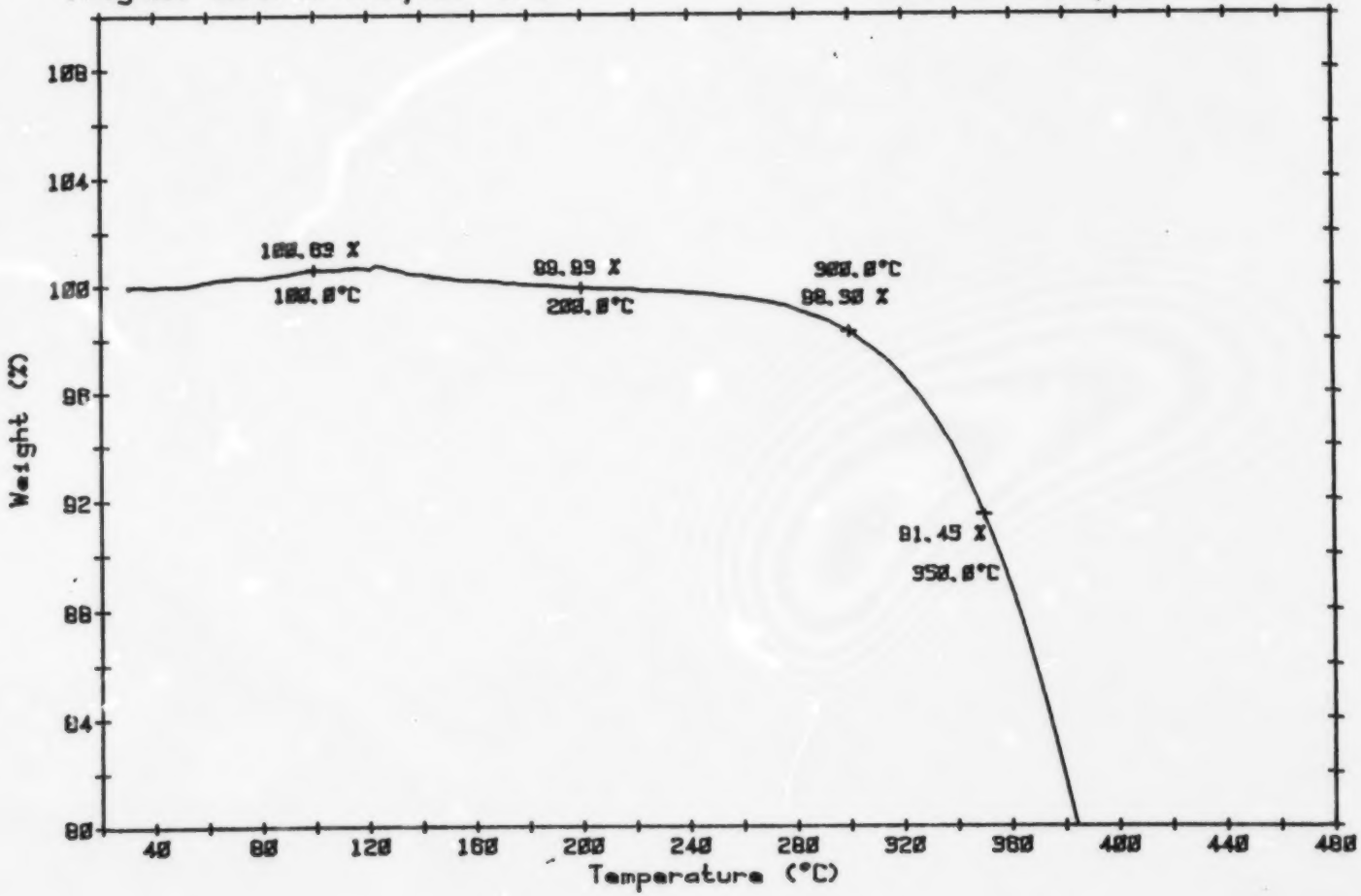
FIGURE 17

36-88

TGA

Sample: SF-881422 KOCH 85/100
Size: 6.77 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0

Date: 8-Sep-88 Time: 15:18:59
File: SQ.06 42
Operator: AI PT MESH
Plotted: 29-Sep-88 15:16:31



DuPont 1090

FIGURE 18

35-98

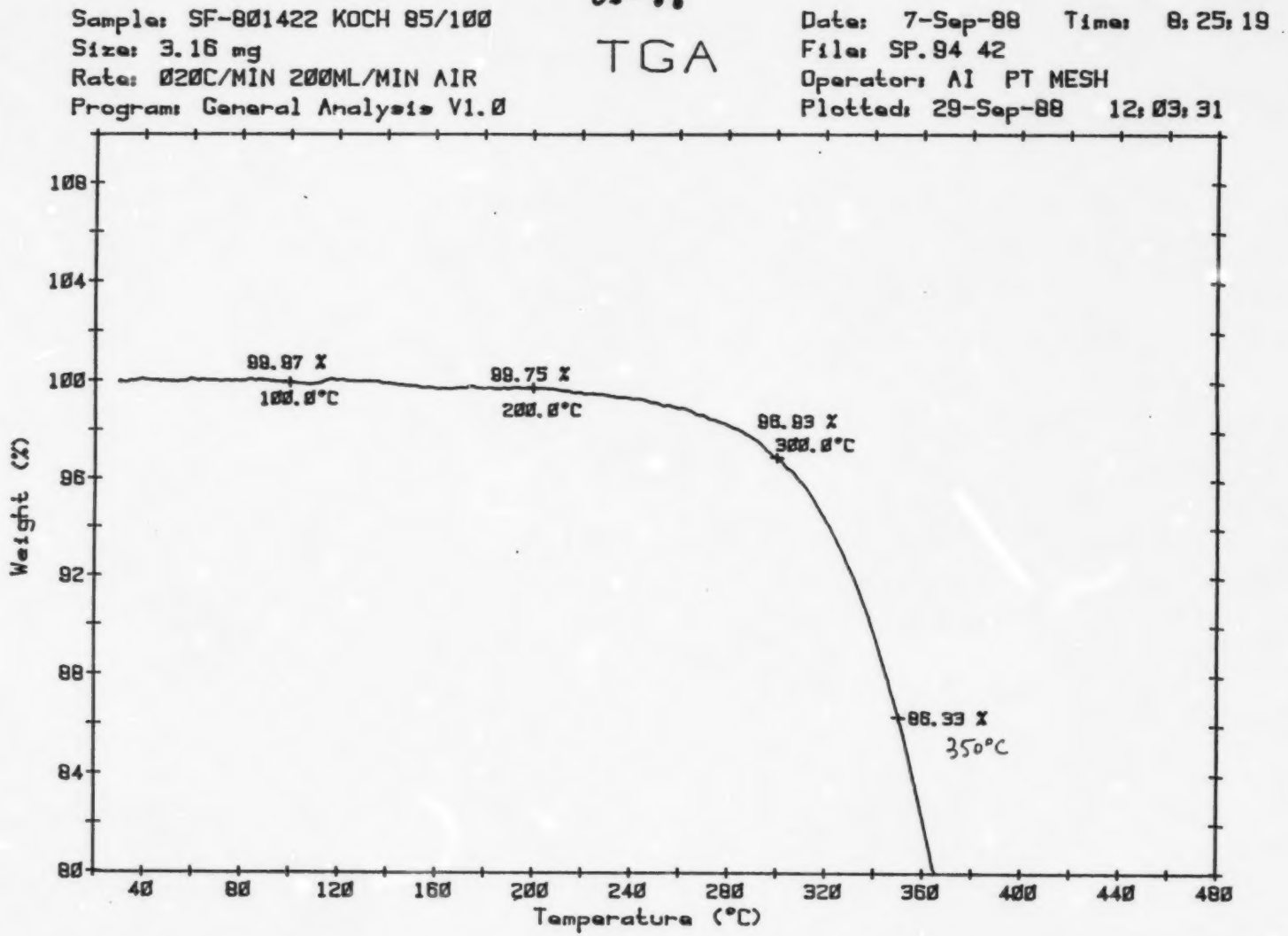


FIGURE 19

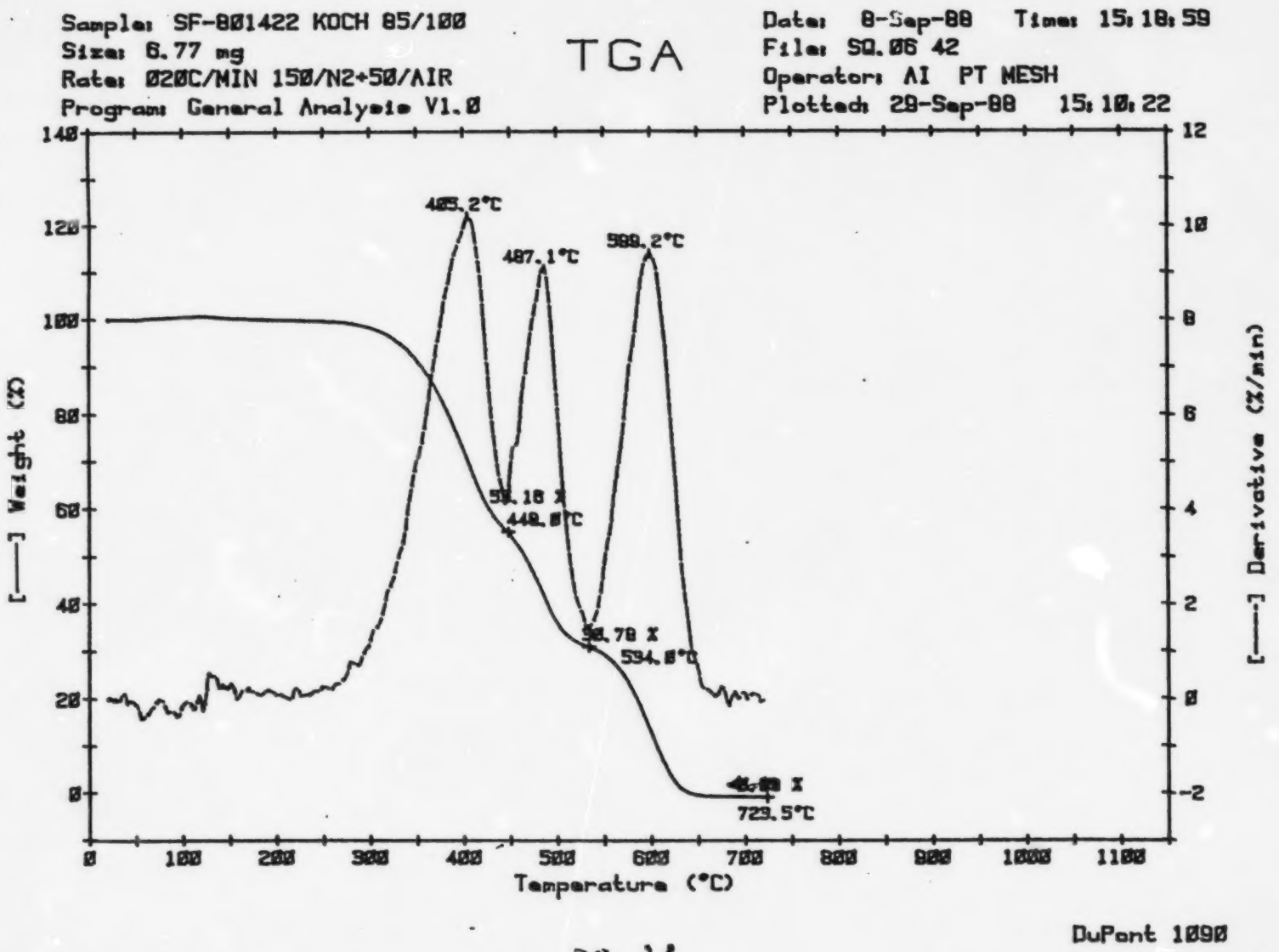
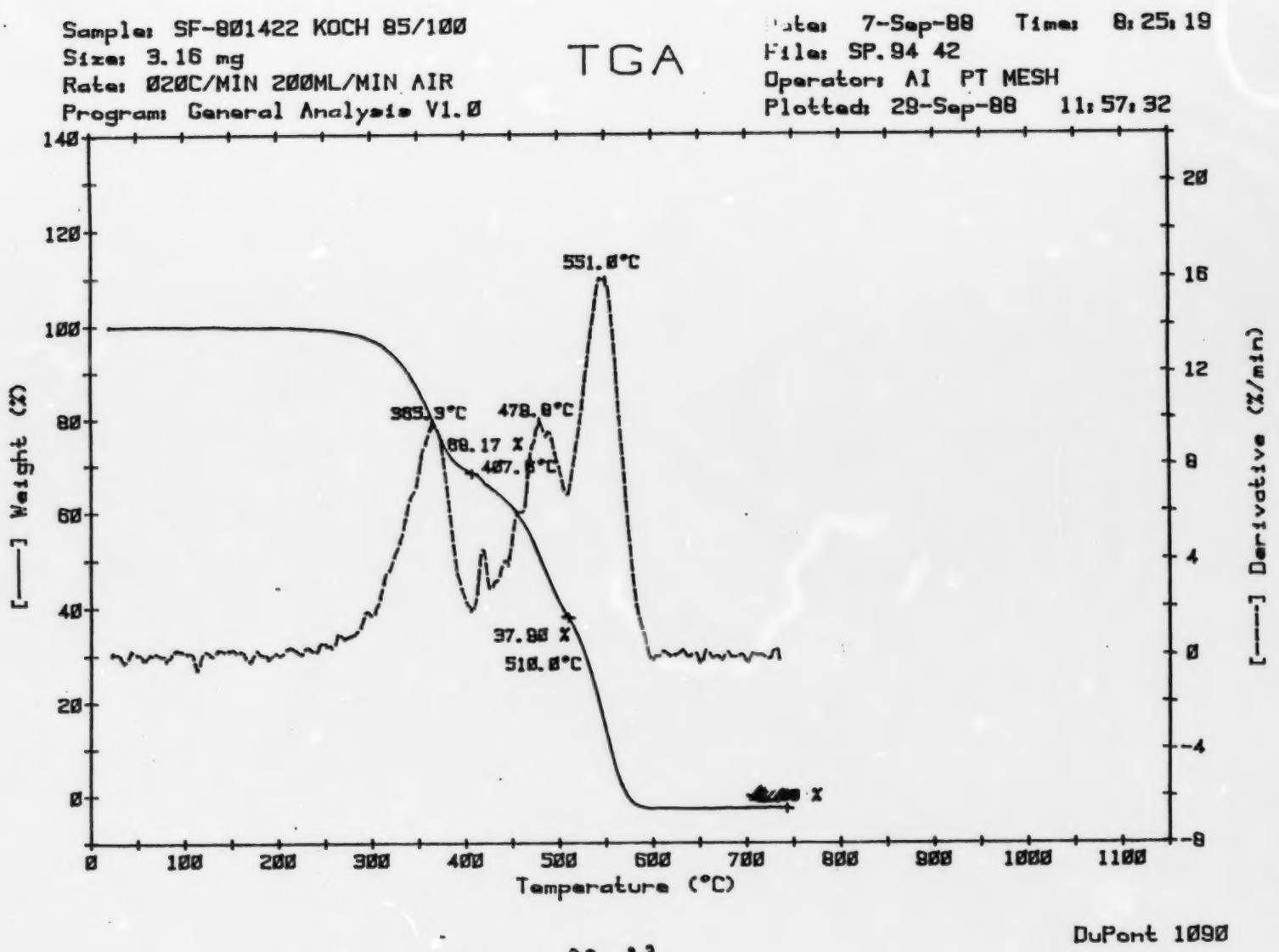

Sample: SF-881422 KOCH 85/100
Size: 6.77 mg
Rate: 020C/MIN 150/N2+50/AIR
Program: General Analysis V1.0
TGA
Date: 8-Sep-88 Time: 15:18:59
File: SQ.06 42
Operator: AI PT MESH
Plotted: 29-Sep-88 15:10:22
485.2°C
487.1°C
588.2°C
449.8°C
594.8°C
723.5°C
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
DuPont 1090

FIGURE 20


Sample: SF-801422 KOCH 85/100
Size: 3.16 mg
Rate: 020C/MIN 200ML/MIN AIR
Program: General Analysis V1.0
TGA
Date: 7-Sep-88 Time: 8:25:19
File: SP.94 42
Operator: AI PT MESH
Plotted: 29-Sep-88 11:57:32
551.0°C
485.3°C
478.0°C
88.17 %
487.0°C
37.80 %
510.0°C
[——] Weight (%)
[——] Derivative (%/min)
Temperature (°C)
DuPont 1090

Appendix 3

Chromatograms of Condensable Hydrocarbons Generated from TGA Simulator

Table 1
BOILING POINTS AND RETENTION TIMES OF C5 TO C44
COMPONENTS OF CALIBRATION STANDARD

Varian Vista Gas Chromatograph with Vista 402 Data Station

Column:	30 m, 0.25 micron film thickness JW DB-1 Capillary
Detector:	FID
Temperature Programmed:	50°C ISO 5 min 5°C/min to 180°C 180°C ISO 45 min
Injection Port:	300°C
Carnier Gas:	Helium 1ml/min
Ionization Temperature:	300°C
Sample Size:	0.2 ml in methylene chlorine

Component	Boiling Point °C	Retention Time minutes
N-C5	36	2.12
N-C6	69	2.44
N-C7	98	3.22
N-C8	126	5.12
N-C9	151	8.43
N-C10	174	12.20
N-C11	196	15.81
N-C12	216	19.18
N-C14	253	25.12
N-C15	271	27.84
N-C16	287	30.41
N-C17	302	32.86
N-C18	317	35.08
N-C20	344	39.40
N-C24	391	47.06
N-C28	432	54.00
N-C32	468	65.29
N-C36	498	91.23
N-C40	525	110.59

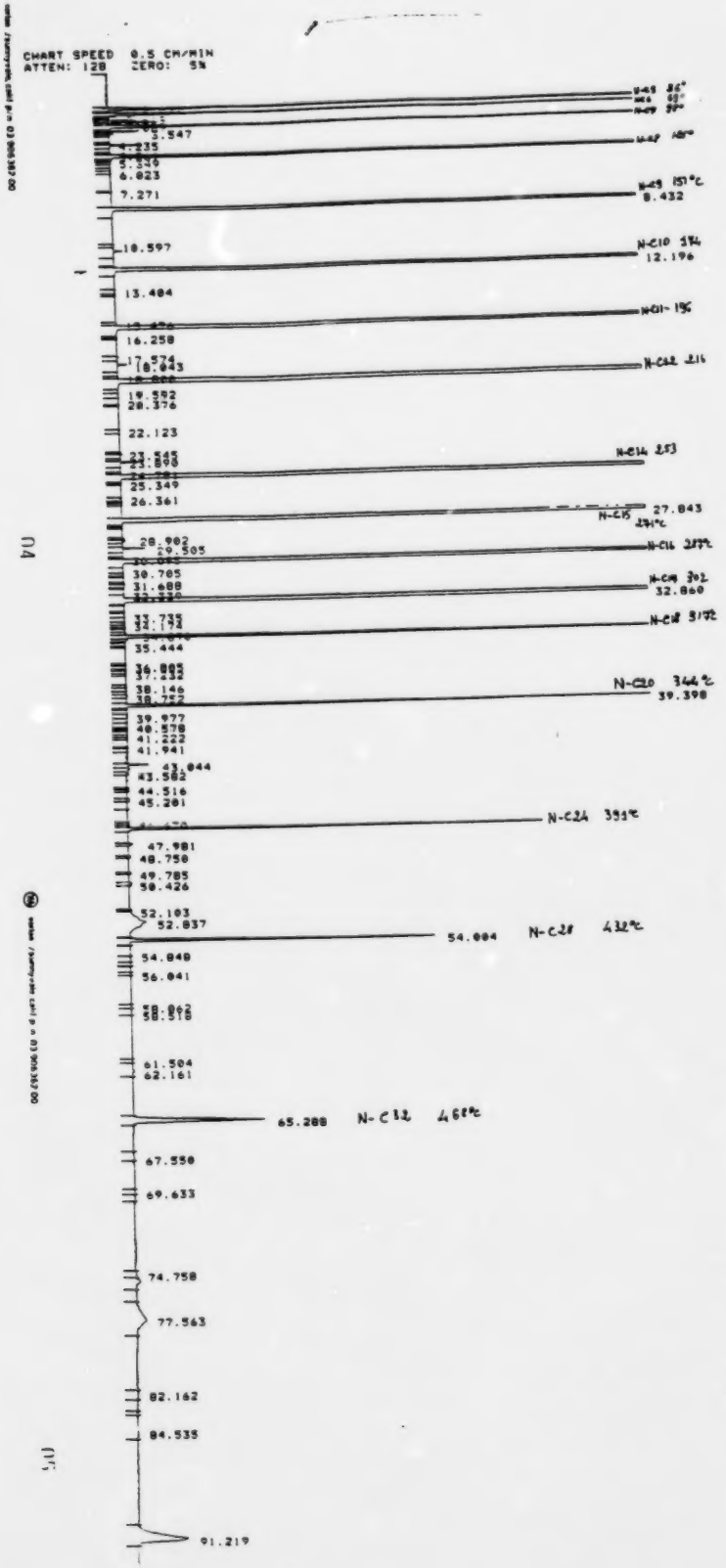


FIGURE 1: CHROMATOGRAM OF CALIBRATION STANDARD

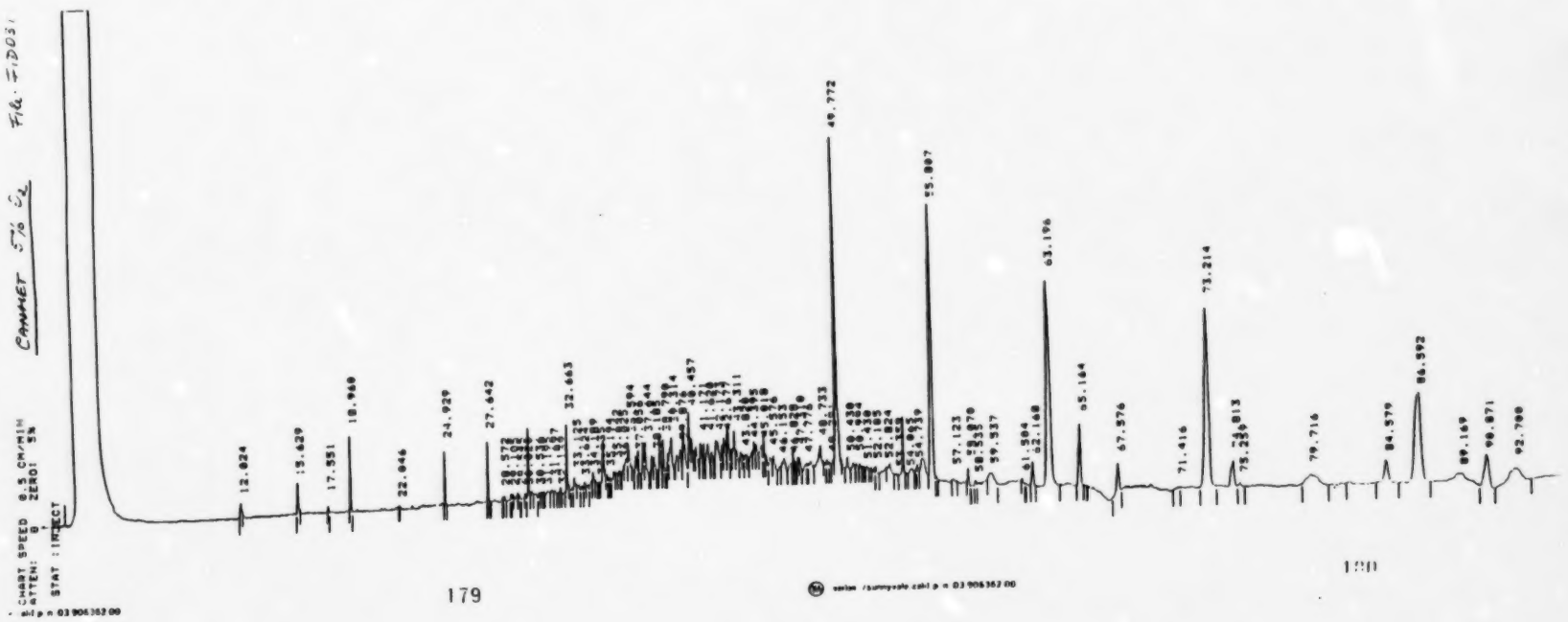


FIGURE 2: SIMULATED TGA TEST WITH CANMET DEMO AT 300°C AND 5% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

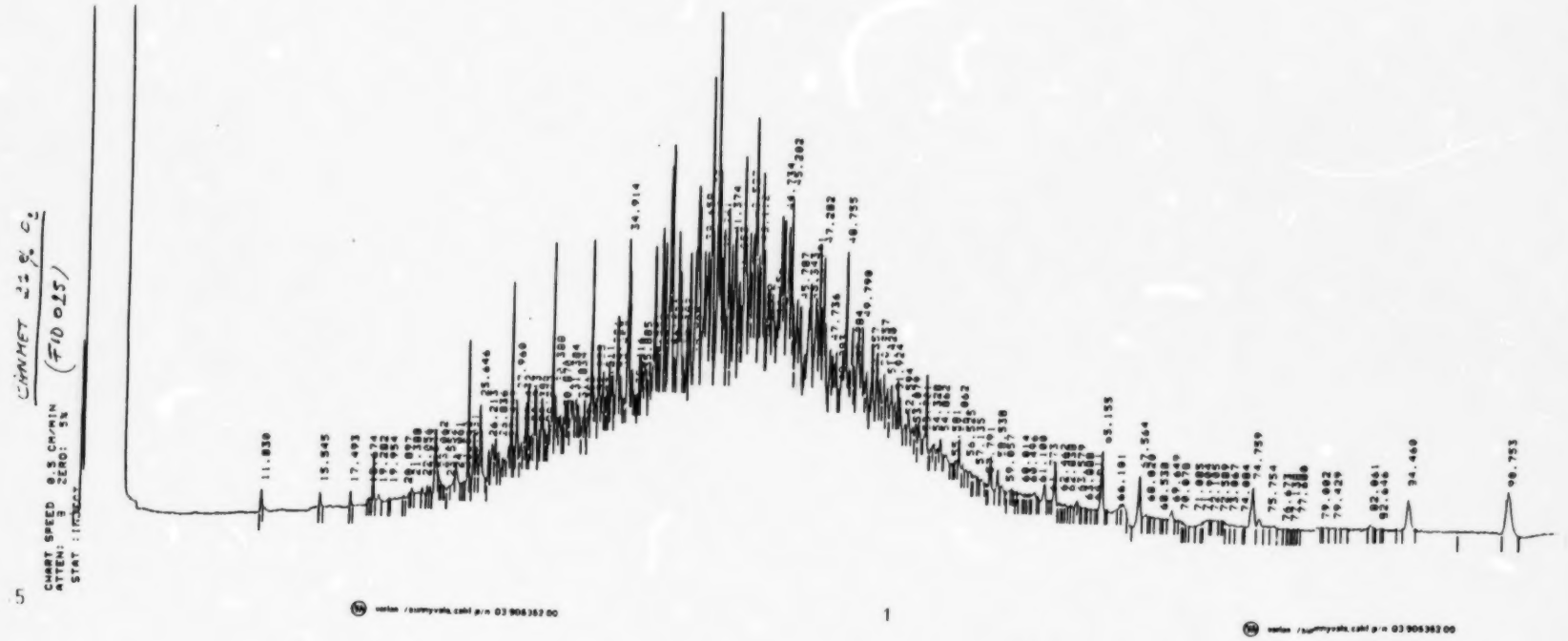


FIGURE 3: SIMULATED TGA TEST WITH CANMET DEMO AT 300^{O}C AND 21% OXYGEN
CHROMATOGRAPH OF CONDENSABLE HYDROCARBONS

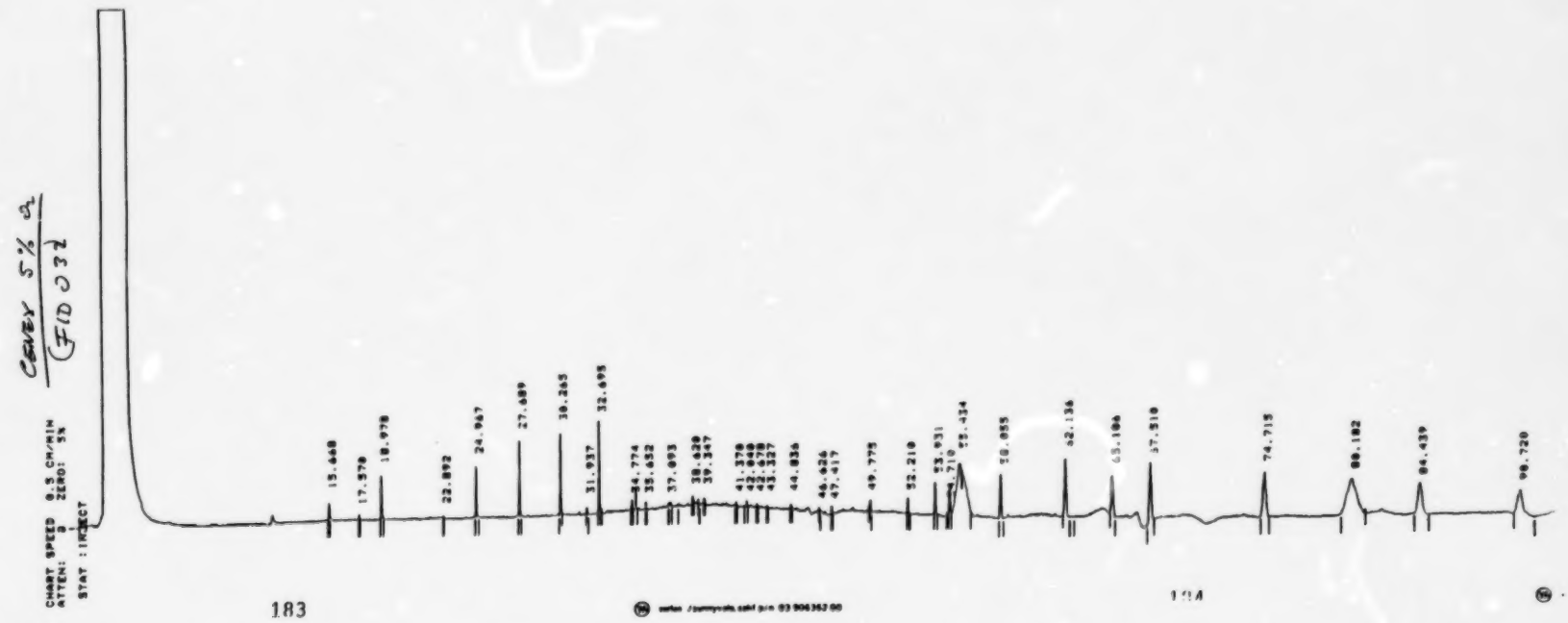


FIGURE 4: SIMULATED TGA TEST WITH CENEX AT 300^{o}C AND 5% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

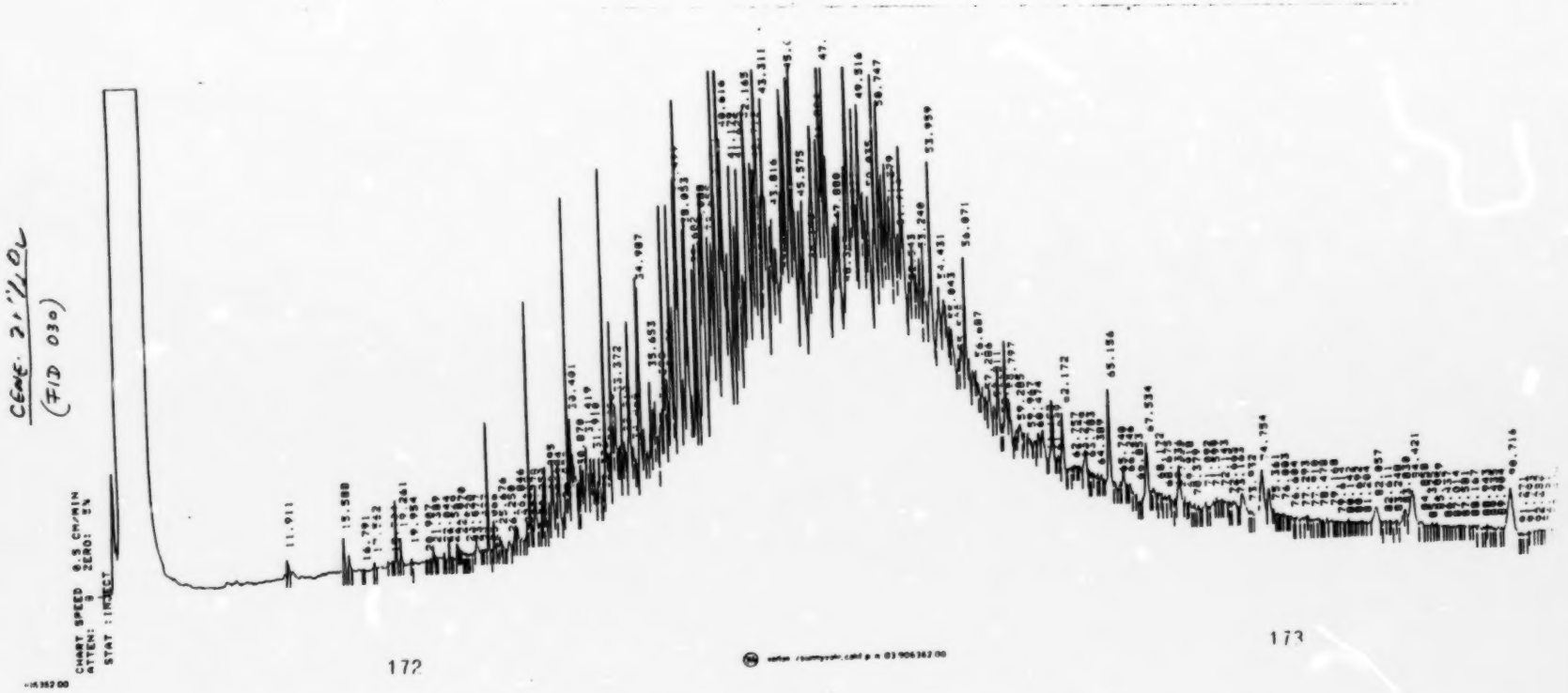


FIGURE 5: SIMULATED TGA TEST WITH CENEX RESIDUUM AT 300°C AND 21% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

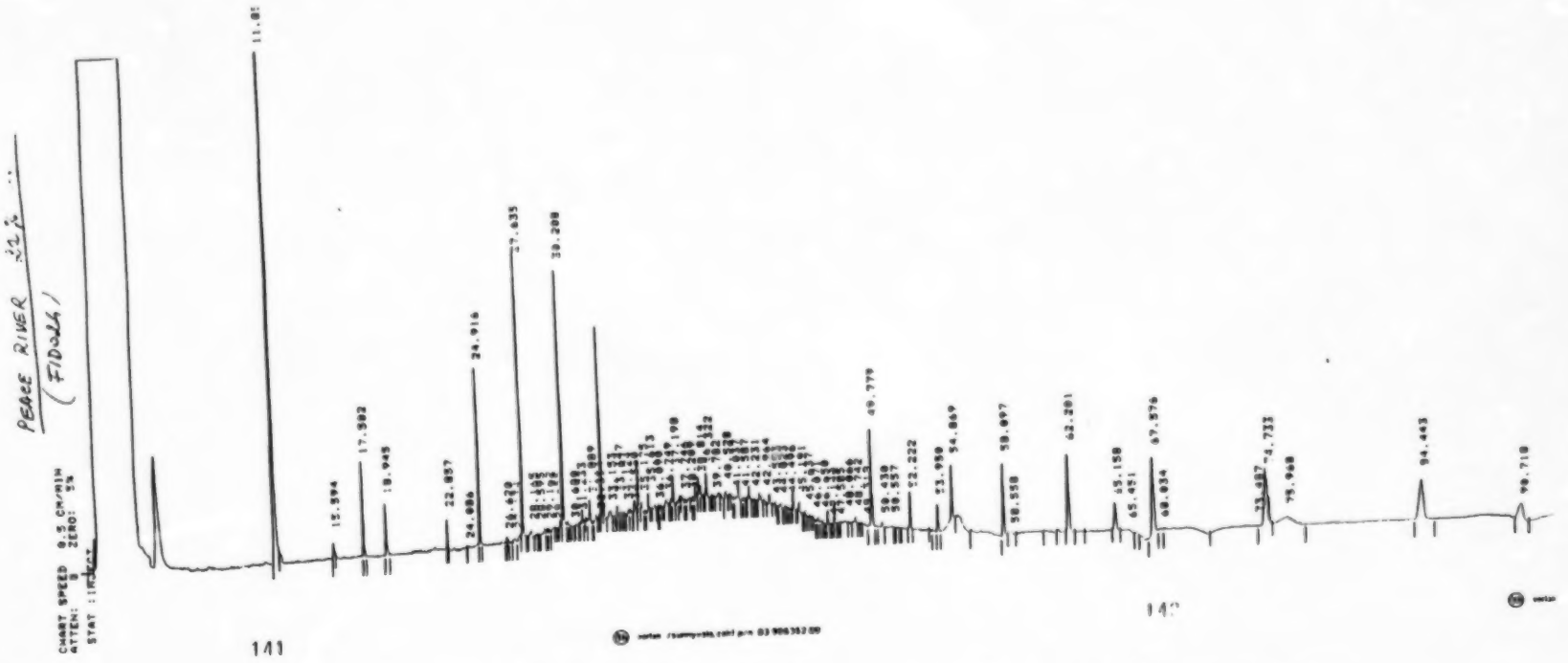


FIGURE 6: SIMULATED TGA TEST WITH PEACE RIVER RESIDUUM AT 300^{o}C AND 5% OXYGEN
CHORMATOGRAM OF CONDENSABLE HYDROCARBONS

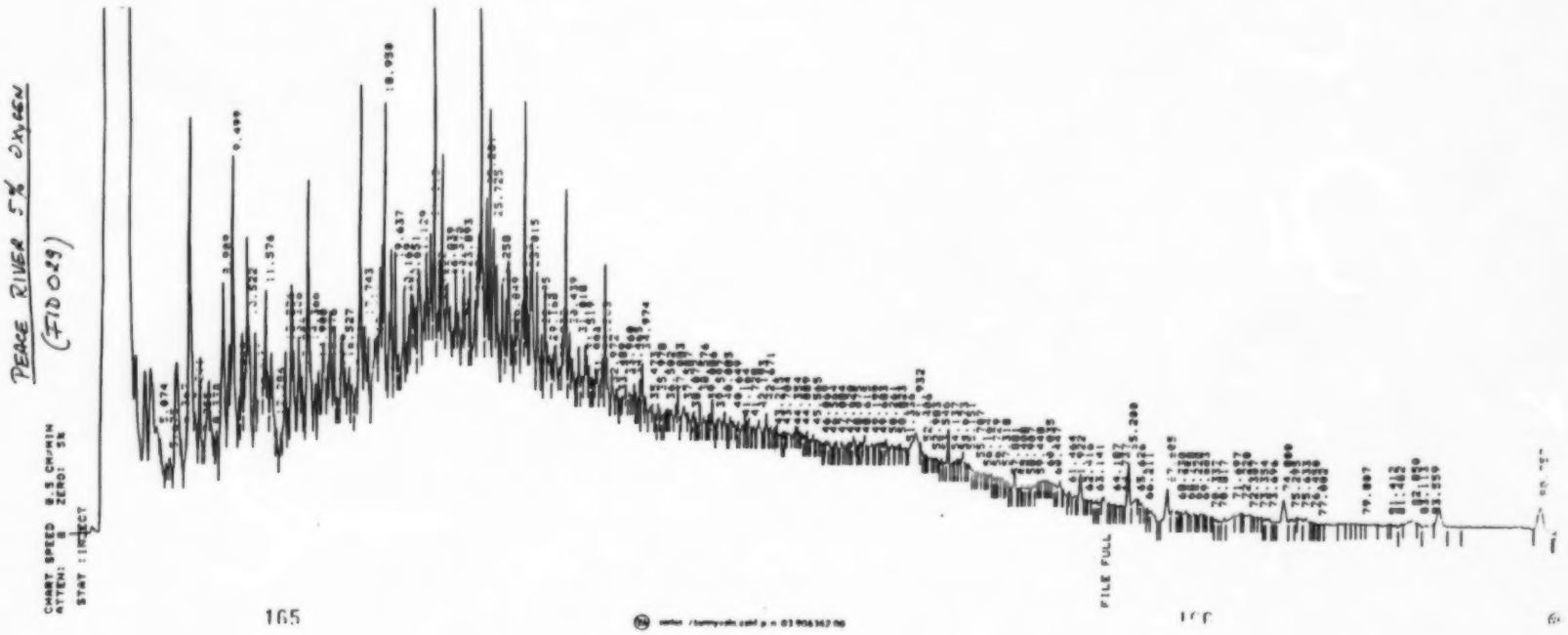


FIGURE 7: SIMULATED TGA TEST WITH PEACE RIVER RESIDUUM AT 300°C AND 21% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

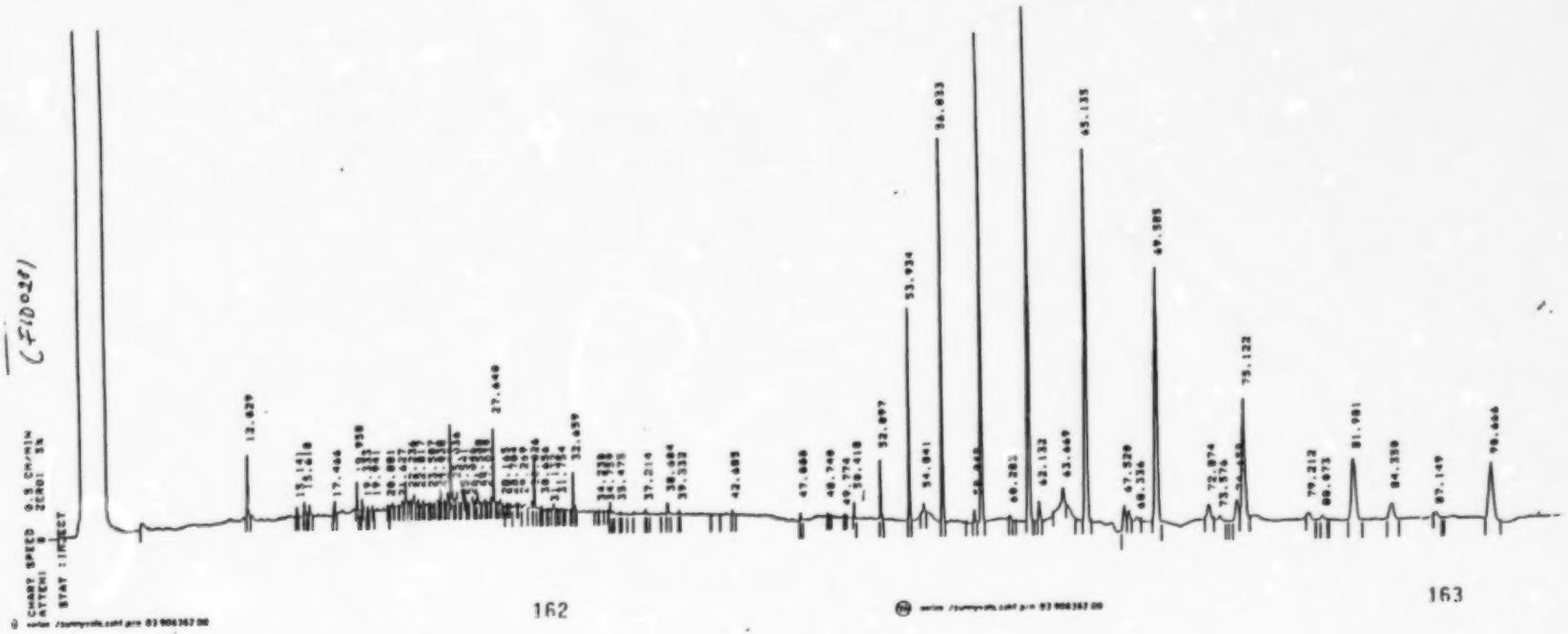


FIGURE 8: SIMULATED TGA TEST WITH KOCH 85/100 RESIDUUM AT 300°C AND 5% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

FIGURE 9: SIMULATED TGA TEST WITH KOCH 85/100 RESIDUUM AT 300°C AND 21% OXYGEN CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

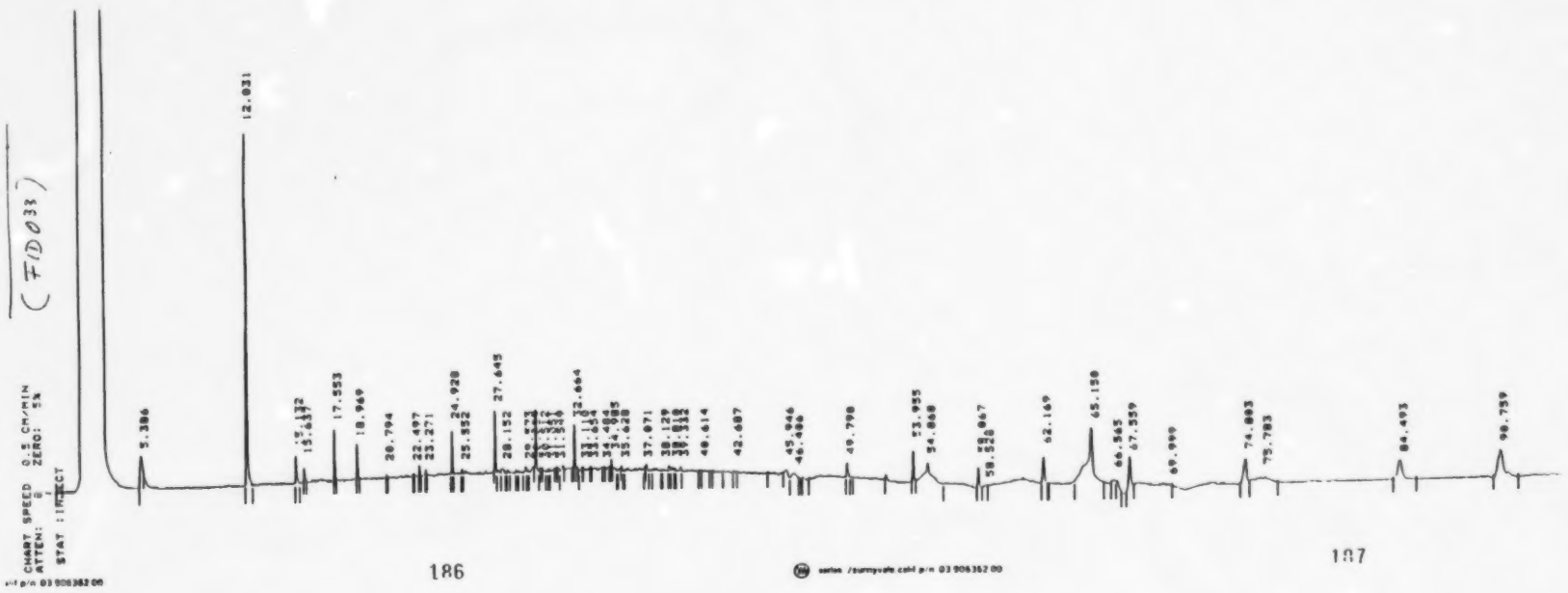


FIGURE 10: SIMULATED TGA TEST WITH SUNCOR RESIDUUM AT 300°C AND 5% OXYGEN CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

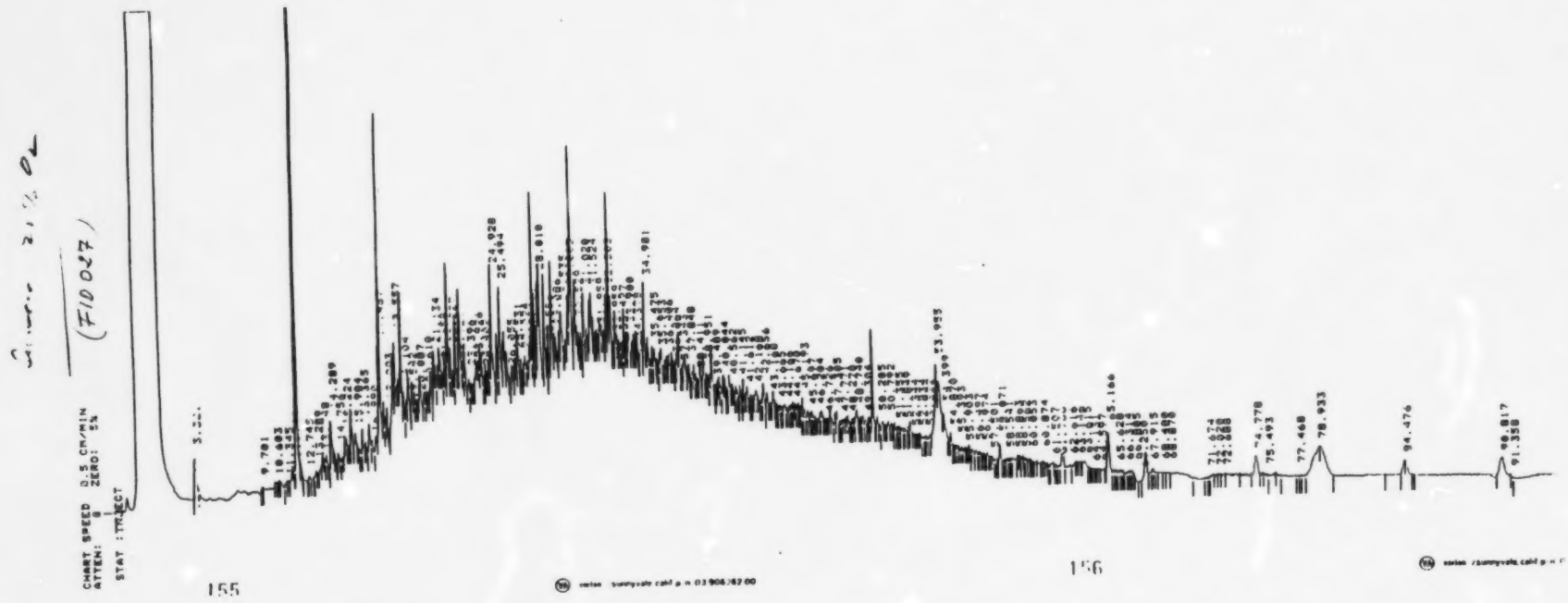


FIGURE 11: SIMULATED TGA TEST WITH SUNCOR RESIDUUM AT 300^{o}C AND 21% OXYGEN
CHROMATOGRAM OF CONDENSABLE HYDROCARBONS

Appendix 4

Pore Volume and Pore Size Distributions of Feeds and Products

Sample Calculations for Determining Pore Volume and Pore Distributions with 1000Å Upper Limit

The pore volumes and pore distributions presented in this Appendix are not determined on the same basis for each coal and its products. In order to do a meaningful comparison, only pores of 1000Å or less were considered. The following sample calculations using the Obed feed data indicate how this was done.

Total Pore Volume less than 1000Å:

Cum. pore volume for pores having 1000Å in their range (row 1)
= A = 0.001645

Pore volume contributed by pores greater than 1000Å

$$= B = \frac{3033.7 - 1000}{3033.7 - 880.9} \times A$$
$$= 0.9447 \times 0.001645$$
$$= 0.001554 \text{ cc/g}$$

Total volume of pores less than 1000Å
= C = Total pore volume (row 23) - B
= 0.008052 - 0.001554
= 0.006498 cc/g

Pore Volume Contributed by Micro-Pores (0-20Å):

Pore volume contributed by pores greater than 20Å and having 20Å pores in their range (row 19)

$$= D = \frac{20.1 - 20.0}{20.1 - 19.1} \times 0.000112$$
$$= 0.1 \times 0.000112$$
$$= 0.000011 \text{ cc/g}$$

Pore volume contributed by all pores greater than 20Å
= E = row 18 + D
= 0.007494 + 0.00011
= 0.007505 cc/g

Pore volume contributed by pores less than 20Å

= F = row 23 - E

= 0.008052 - 0.007505

= 0.000547 cc/g

% of total pore volume contributed by micro-pores

$= G = \frac{F}{C}$

$= \frac{0.000547}{0.006498} \times 100$

= 8.4

Pore Volume contributed by meso-pores (20Å to 200Å):

Pore volume of all pores greater than 20Å minus pore volume of all pores greater than 200Å

$= H = E - (\frac{207.6 - 200.0}{207.6 - 139.8} \times 0.000657 + 0.004173)$

= 0.007505 - (0.1121 x 0.000657 + 0.004173

= 0.007505 - 0.004247

= 0.003258 cc/g

% of total pore volume contributed by meso-pores

$= I = \frac{H}{C}$

$= \frac{0.003258}{0.006498} \times 100$

= 50.1

Pore Volume Contributed by Meso-Pores (200Å - 1000Å):

Pore volume of macro-pores

= J = C - (H + F)

= 0.006498 - (0.003258 + 0.000547)

= 0.002693 cc/g

% of total pore volume contributed by macro-pores

= K = 100 - (G + I)

= 100 - 58.5

= 41.5

CMRC SAMPLE #OBED FEED

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 3033.7-880.9	1047.7	0.001645	0.001645
2 880.9-739.3	797.1	0.000315	0.001960
3 739.3-698.4	716.5	0.000101	0.002061
4 698.4-518.8	580.8	0.000591	0.002652
5 518.8-403.9	445.1	0.000326	0.002978
6 403.9-207.6	243.3	0.001195	0.004173
7 207.6-139.8	158.0	0.000657	0.004830
8 139.8-107.2	117.7	0.000400	0.005230
9 107.2-96.0	93.2	0.000287	0.005517
10 86.0-71.7	76.7	0.000276	0.005793
11 71.7-60.8	64.7	0.000254	0.006047
12 60.8-53.5	56.1	0.000180	0.006227
13 53.5-43.3	46.7	0.000231	0.006458
14 43.3-34.5	37.1	0.000295	0.006753
15 34.5-24.7	26.9	0.000504	0.007257
16 24.7-22.0	22.3	0.000073	0.007330
17 22.0-21.0	21.4	0.000056	0.007386
18 21.0-20.1	20.4	0.000108	0.007494
19 20.1-19.1	19.5	0.000112	0.007606
20 19.1-18.2	18.5	0.000128	0.007734
21 18.2-17.3	17.6	0.000104	0.007838
22 17.3-16.2	16.6	0.000101	0.007939
23 16.2-15.6	15.7	0.000113	0.008052

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.008237 CC/G

OB-D350 NITROGEN
STATION 3 STARTED 3/ 4/89 16:58 COMPLETED 3/ 5/89 13: 9

ADSORPTION PORE VOLUME AND PORE AREA DISTRIBUTIONS

PORE DIA. RANGE, A	AVERAGE DIA.,A	PORE VOLUME (CC/G)	CUMULATIVE PORE VOLUME	PORE AREA (SQ M/G)	CUMULATIVE PORE AREA
2825.1-1746.3	2025.7	0.001273	0.001273	0.025	0.025
1746.3-1151.5	1327.9	0.001291	0.002564	0.039	0.064
1151.5- 884.9	980.6	0.000609	0.003174	0.025	0.089
884.9- 757.7	809.6	0.000573	0.003747	0.028	0.117
757.7- 599.4	658.7	0.000644	0.004391	0.039	0.156
599.4- 514.7	549.1	0.000331	0.004722	0.024	0.180
514.7- 482.3	496.5	0.000290	0.005012	0.023	0.204
482.3- 436.0	456.3	0.000225	0.005237	0.020	0.224
436.0- 392.6	411.4	0.000241	0.005478	0.023	0.247
392.6- 216.4	253.4	0.001595	0.007073	0.252	0.499
216.4- 107.8	125.3	0.001300	0.008373	0.415	0.914
107.8- 69.2	78.2	0.000585	0.008958	0.299	1.213
69.2- 50.6	55.8	0.000309	0.009267	0.221	1.435
50.6- 32.5	36.4	0.000411	0.009678	0.452	1.886
32.5- 21.3	23.5	0.000275	0.009953	0.469	2.356
21.3- 18.5	18.9	0.000032	0.009985	0.068	2.424
18.5- 17.6	17.9	0.000022	0.010007	0.049	2.473
17.6- 16.6	17.0	0.000037	0.010043	0.086	2.559
16.6- 15.7	16.0	0.000028	0.010072	0.071	2.630
15.7- 14.8	15.1	0.000030	0.010102	0.080	2.709
14.8- 13.7	14.1	0.000031	0.010133	0.088	2.798
13.7- 12.8	13.1	0.000044	0.010177	0.133	2.931
12.8- 11.7	12.1	0.000048	0.010224	0.159	3.089

LIQUID EQUIVALENT OF MAXIMUM VOLUME SORBED: 0.010078 CC/G

CMRC SAMPLE #O-L-KO

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2593.6-952.1	1150.8	0.000408	0.000408
2 952.1-815.7	873.0	0.000055	0.000463
3 815.7-651.7	714.0	0.000051	0.000514
4 651.7-490.7	546.8	0.000095	0.000609
5 490.7-382.3	421.3	0.000061	0.000670
6 382.3-206.8	242.4	0.000141	0.000811
7 206.8-136.8	155.5	0.000089	0.000900
8 136.8-102.1	112.9	0.000079	0.000979
9 102.1-81.4	88.4	0.000051	0.001030
10 81.4-67.1	72.1	0.000040	0.001070
11 67.1-56.5	60.3	0.000051	0.001121
12 56.5-48.6	51.4	0.000045	0.001166
13 48.6-37.9	41.3	0.000040	0.001206
14 37.9-29.6	32.1	0.000062	0.001268
15 29.6-20.0	22.2	0.000103	0.001371
16 20.0-16.4	16.8	0.000019	0.001390
17 16.4-15.5	15.8	0.000015	0.001405
18 15.5-14.6	14.9	0.000009	0.001414
19 14.6-13.6	14.0	0.000012	0.001426
20 13.6-12.6	13.0	0.000010	0.001436
21 12.6-11.6	12.0	0.000021	0.001457
22 11.6-10.5	10.9	0.000021	0.001478

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.001481 CC/G

CMRC SAMPLE #O-L-CE

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 3130.5-1019.6	1226.4	0.000494	0.000494
2 1019.6-902.9	884.7	0.000055	0.000549
3 802.9-648.5	707.6	0.000062	0.000611
4 648.5-489.6	545.3	0.000091	0.000702
5 489.6-383.9	422.2	0.000056	0.000758
6 383.9-206.2	241.8	0.000131	0.000889
7 206.2-136.1	154.7	0.000103	0.000992
8 136.1-102.0	112.7	0.000080	0.001072
9 102.0-80.5	87.7	0.000058	0.001130
10 80.5-67.1	71.8	0.000050	0.001180
11 67.1-56.3	60.1	0.000025	0.001205
12 56.3-48.5	51.3	0.000086	0.001291
13 48.5-37.7	41.2	0.000043	0.001334
14 37.7-29.5	31.9	0.000059	0.001393
15 29.5-19.9	22.0	0.000075	0.001468
16 19.9-17.1	17.5	0.000005	0.001473
17 17.1-16.2	16.5	0.000014	0.001487
18 16.2-15.3	15.6	0.000015	0.001502
19 15.3-14.3	14.6	0.000008	0.001510
20 14.3-13.4	13.7	0.000010	0.001520
21 13.4-12.4	12.7	0.000015	0.001535
22 12.4-11.4	11.7	0.000017	0.001552
23 11.4-10.2	10.5	0.000025	0.001577

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.001587 CC/G

CMRC SAMPLE #0-H-PR

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2942.8-876.4	1049.8	0.002223	0.002223
2 876.4-757.6	808.0	0.000216	0.002439
3 757.6-620.8	674.4	0.000220	0.002659
4 620.8-472.3	524.9	0.000263	0.002922
5 472.3-388.3	420.5	0.000112	0.003034
6 388.3-208.2	244.4	0.000249	0.003283
7 208.2-137.8	156.7	0.000207	0.003490
8 137.8-100.4	111.8	0.000094	0.003584
9 100.4-80.5	87.3	0.000115	0.003699
10 80.5-65.4	70.6	0.000069	0.003768
11 65.4-55.8	59.2	0.000084	0.003852
12 55.8-47.4	50.4	0.000011	0.003863
13 47.4-36.9	40.3	0.000144	0.004007
14 36.9-28.9	31.3	0.000081	0.004088
15 28.9-19.1	21.3	0.000182	0.004270
16 19.1-16.3	16.7	0.000012	0.004282
17 16.3-15.4	15.7	0.000021	0.004303
18 15.4-14.5	14.8	0.000007	0.004310
19 14.5-13.5	13.9	0.000027	0.004337
20 13.5-12.6	12.9	0.000010	0.004347
21 12.6-11.6	11.9	0.000020	0.004367
22 11.6-10.6	10.9	0.000020	0.004387
23 10.6-9.5	9.9	0.000021	0.004408

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.004541 CC/G

CMRC SAMPLE #0-L-PR

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2075.4-1147.3	1369.3	0.000876	0.000876
2 1147.3-908.1	999.1	0.000171	0.001047
3 908.1-706.0	779.9	0.000146	0.001193
4 706.0-527.3	589.0	0.000130	0.001323
5 527.3-387.9	434.6	0.000086	0.001409
6 387.9-206.3	242.0	0.000192	0.001601
7 206.3-138.5	156.9	0.000089	0.001690
8 138.5-102.4	113.6	0.000068	0.001758
9 102.4-81.8	88.8	0.000047	0.001805
10 81.8-67.4	72.5	0.000027	0.001832
11 67.4-56.7	60.5	0.000061	0.001893
12 56.7-48.7	51.6	0.000058	0.001951
13 48.7-38.2	41.6	0.000032	0.001983
14 38.2-30.0	32.4	0.000033	0.002016
15 30.0-20.3	22.5	0.000091	0.002107
16 20.3-17.6	17.9	0.000015	0.002122
17 17.6-16.6	17.0	0.000002	0.002124
18 16.6-15.7	16.0	0.000007	0.002131
19 15.7-14.8	15.1	0.000021	0.002152
20 14.8-13.8	14.2	0.000008	0.002160
21 13.8-12.8	13.2	0.000009	0.002169
22 12.8-11.9	12.2	0.000024	0.002193
23 11.9-10.7	11.1	0.000018	0.002211

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.002240 CC/G

CMRC SAMPLE #O-L-SH

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2899.4-893.0	1075.5	0.001743	0.001743
2 893.0-767.3	820.3	0.000205	0.001948
3 767.3-595.2	658.1	0.000232	0.002180
4 595.2-530.2	557.4	0.000126	0.002306
5 530.2-392.9	439.9	0.000141	0.002447
6 392.9-205.5	241.4	0.000273	0.002720
7 205.5-136.0	154.6	0.000115	0.002835
8 136.0-101.1	112.1	0.000107	0.002942
9 101.1-79.3	86.6	0.000084	0.003026
10 79.3-65.4	70.2	0.000046	0.003072
11 65.4-55.9	59.3	0.000042	0.003114
12 55.9-47.6	50.6	0.000086	0.003200
13 47.6-37.2	40.6	0.000079	0.003279
14 37.2-28.8	31.3	0.000098	0.003377
15 28.8-18.9	21.1	0.000164	0.003541
16 18.9-16.2	16.5	0.000019	0.003560
17 16.2-15.2	15.6	0.000021	0.003581
18 15.2-14.3	14.6	0.000012	0.003593
19 14.3-13.4	13.7	0.000013	0.003606
20 13.4-12.4	12.8	0.000009	0.003615
21 12.4-11.4	11.8	0.000012	0.003627
22 11.4-10.4	10.8	0.000018	0.003645
23 10.4-9.3	9.7	0.000016	0.003661

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.003751 CC/G

CMRC SAMPLE #O-H-CD

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2324.2-827.8	988.9	0.003117	0.003117
2 827.8-706.9	757.4	0.000354	0.003471
3 706.9-624.3	659.4	0.000270	0.003741
4 624.3-481.6	533.3	0.000412	0.004153
5 481.6-367.9	407.9	0.000448	0.004601
6 367.9-199.0	233.1	0.000849	0.005450
7 199.0-135.6	153.2	0.000329	0.005779
8 135.6-101.4	112.2	0.000189	0.005968
9 101.4-80.9	87.9	0.000124	0.006092
10 80.9-66.7	71.7	0.000088	0.006180
11 66.7-56.2	59.9	0.000088	0.006268
12 56.2-48.3	51.2	0.000063	0.006331
13 48.3-37.9	41.3	0.000074	0.006405
14 37.9-29.8	32.2	0.000078	0.006483
15 29.8-20.0	22.2	0.000124	0.006607
16 20.0-17.2	17.5	0.000013	0.006620
17 17.2-16.3	16.6	0.000010	0.006630
18 16.3-15.3	15.7	0.000014	0.006644
19 15.3-14.4	14.7	0.000017	0.006661
20 14.4-13.4	13.8	0.000019	0.006680
21 13.4-12.4	12.8	0.000019	0.006699
22 12.4-11.4	11.8	0.000028	0.006727
23 11.4-10.3	10.7	0.000033	0.006760

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.006792 CC/G

CMRC SAMPLE #O-L-CD

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2816.3-854.8	1028.9	0.003072	0.003072
2 854.8-721.6	776.5	0.000318	0.003390
3 721.6-610.3	655.4	0.000289	0.003679
4 610.3-494.2	538.8	0.000353	0.004032
5 494.2-390.8	429.0	0.000324	0.004356
6 390.8-202.4	237.8	0.000502	0.004858
7 202.4-134.8	153.0	0.000127	0.004985
8 134.8-101.3	111.9	0.000081	0.005066
9 101.3-80.5	87.6	0.000049	0.005115
10 80.5-66.5	71.4	0.000050	0.005165
11 66.5-55.9	59.7	0.000046	0.005211
12 55.9-48.1	50.9	0.000044	0.005255
13 48.1-37.9	41.3	0.000051	0.005306
14 37.9-29.6	32.1	0.000054	0.005360
15 29.6-19.7	21.9	0.000113	0.005473
16 19.7-16.9	17.3	0.000024	0.005497
17 16.9-15.1	15.4	0.000009	0.005506
18 15.1-14.1	14.4	0.000013	0.005519
19 14.1-13.2	13.5	0.000010	0.005529
20 13.2-12.2	12.5	0.000012	0.005541
21 12.2-11.2	11.5	0.000021	0.005562
22 11.2-10.1	10.4	0.000025	0.005587

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.005784 CC/G

CMRC SAMPLE #HIGHVALE FEED

0 PORE DIAM. RANGE(A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 3353.0-769.9	893.2	0.005910	0.005910
2 769.8-690.8	725.8	0.000383	0.006293
3 690.8-583.2	626.9	0.000862	0.007155
4 583.2-478.8	519.4	0.000730	0.007885
5 478.8-213.2	250.2	0.003899	0.011784
6 213.2-142.8	161.3	0.001491	0.013275
7 142.8-107.6	118.7	0.000872	0.014147
8 107.6-86.2	93.4	0.000693	0.014840
9 86.2-71.6	76.7	0.000431	0.015271
10 71.3-60.9	64.7	0.000415	0.015686
11 60.9-52.8	55.7	0.000336	0.016022
12 52.8-43.3	46.5	0.000444	0.016466
13 43.3-34.3	37.0	0.000496	0.016962
14 34.3-24.6	26.7	0.000853	0.017815
15 24.6-21.8	22.2	0.000066	0.017881
16 21.8-20.9	21.2	0.000077	0.017958
17 20.9-20.0	20.3	0.000110	0.018068
18 20.0-19.1	19.4	0.000064	0.018132
19 19.1-18.1	18.4	0.000067	0.018199
20 18.1-17.1	17.4	0.000087	0.018286
21 17.1-16.2	16.5	0.000071	0.018357
22 16.2-15.0	15.4	0.000189	0.018546

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.018389 CC/G

CMRC SAMPLE #HIGHVALE 380

0 PORE DIAM. RANGE(A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 4405.1-847.6	968.3	0.007680	0.007680
2 847.6-725.3	776.5	0.000730	0.008410
3 725.3-621.0	663.9	0.001196	0.009606
4 621.0-477.8	529.3	0.001403	0.011009
5 477.8-390.7	423.9	0.001214	0.012223
6 390.7-210.3	246.1	0.003621	0.015844
7 210.3-141.3	159.9	0.001651	0.017495
8 141.3-105.3	116.5	0.001102	0.018597
9 105.3-85.5	92.2	0.000566	0.019163
10 85.5-70.4	75.6	0.000476	0.019639
11 70.4-60.0	63.7	0.000416	0.020055
12 60.0-52.5	55.2	0.000247	0.020302
13 52.5-42.7	46.0	0.000363	0.020665
14 42.7-33.6	36.3	0.000398	0.021063
15 33.6-23.8	26.0	0.000562	0.021625
16 23.8-21.1	21.4	0.000062	0.021687
17 21.1-20.1	20.5	0.000061	0.021748
18 20.1-19.2	19.5	0.000118	0.021866
19 19.2-18.3	18.6	0.000090	0.021956
20 18.3-17.3	17.6	0.000058	0.022014
21 17.3-17.0	17.0	0.000054	0.022068
22 17.0-15.4	16.0	0.000185	0.022253
23 15.4-14.4	14.6	0.001792	0.024045

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.023636 CC/G

CMRC SAMPLE #H-H-CD

0 PORE DIAM. RANGE (A)	1 AVE. PORE DIAM. (A)	2 INCR. PORE VOL.(cc/g)	3 CUM. PORE VOL.(cc/g)
1 2628.2-908.9	1096.4	0.004967	0.004967
2 908.9-702.5	778.4	0.001226	0.006193
3 702.5-676.0	687.0	0.000309	0.006502
4 676.0-473.3	537.8	0.001359	0.007861
5 473.3-454.8	461.5	0.000187	0.008048
6 454.8-204.5	240.7	0.003422	0.011470
7 204.5-139.1	156.9	0.001029	0.012499
8 139.1-103.9	115.0	0.000548	0.013047
9 103.9-81.8	89.2	0.000314	0.013361
10 81.8-66.8	72.0	0.000175	0.013536
11 66.8-56.3	60.0	0.000175	0.013711
12 56.3-48.8	51.5	0.000102	0.013813
13 48.8-38.6	41.9	0.000120	0.013933
14 38.6-29.9	32.5	0.000116	0.014049
15 29.9-20.0	22.2	0.000168	0.014217
16 20.0-17.3	17.6	0.000024	0.014241
17 17.3-16.3	16.7	0.000009	0.014250
18 16.3-15.4	15.7	0.000029	0.014279
19 15.4-14.5	14.8	0.000027	0.014306
20 14.5-13.5	13.9	0.000011	0.014317
21 13.5-12.5	12.9	0.000023	0.014340
22 12.5-11.4	11.8	0.000056	0.014396
23 11.4-10.3	10.7	0.000046	0.014442

LIQUID EQUIVALENT OF MAXIMUM VOL. SORBED = 0.014676 CC/G

H-L-CD NITROGEN
STATION 1 STARTED 3/ 4/89 16:58 COMPLETED 3/ 5/89 2:45

ADSORPTION PORE VOLUME AND PORE AREA DISTRIBUTIONS

PORE DIA. RANGE, A	AVERAGE DIA.,A	PORE VOLUME (CC/G)	CUMULATIVE PORE VOLUME	PORE AREA (SQ M/G)	CUMULATIVE PORE AREA
18785.6-1439.5	1535.2	0.010871	0.010871	0.283	0.283
1439.5-1028.2	1164.7	0.001961	0.012832	0.067	0.351
1028.2- 845.5	916.7	0.001050	0.013881	0.046	0.396
845.5- 694.7	753.8	0.000845	0.014727	0.045	0.441
694.7- 582.7	627.5	0.000989	0.015716	0.063	0.504
582.7- 529.0	552.2	0.000477	0.016193	0.035	0.539
529.0- 510.4	518.8	0.000185	0.016378	0.014	0.553
510.4- 491.3	500.3	0.000745	0.017123	0.060	0.613
491.3- 216.1	254.5	0.004718	0.021841	0.742	1.354
216.1- 106.5	124.0	0.002631	0.024471	0.849	2.203
106.5- 70.9	79.7	0.000831	0.025303	0.417	2.620
70.9- 49.9	55.6	0.000460	0.025762	0.331	2.951
49.9- 31.4	35.3	0.000399	0.026162	0.453	3.404
31.4- 20.3	22.5	0.000257	0.026419	0.459	3.862
20.3- 17.5	17.9	0.000011	0.026430	0.025	3.888
17.5- 16.6	16.9	0.000029	0.026459	0.068	3.956
16.6- 15.7	16.0	0.000015	0.026475	0.038	3.994
15.7- 14.7	15.1	0.000030	0.026505	0.079	4.074
14.7- 13.8	14.1	0.000023	0.026527	0.064	4.138
13.8- 12.8	13.1	0.000040	0.026567	0.122	4.260
12.8- 11.8	12.1	0.000042	0.026609	0.138	4.397
11.8- 10.7	11.1	0.000063	0.026672	0.228	4.625

LIQUID EQUIVALENT OF MAXIMUM VOLUME SORBED: 0.027418 CC/G